Corrosion

IN THIS ISSUE:

Some Auto Corrosion Problems

Pages 9 and 14

CORROSION OF IRON AND TIN
A Symposium

CORROSION CONTROL

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This Month in Corrosion Control . . .

AUTOMOBILE CORROSION takes a heavy toll in the Western Hemisphere, especially in areas subject to a marine, or polluted, or marine polluted atmospheres, or where de-icing salt is used on streets and highways. There are some corrective measures, notably under-coating, that help reduce the damage to the body and underparts. One company's method of applying under-coating is described on Page 9.

IF YOUR AUTOMOBILE has suffered corrosion damage, you will want to read carefully "A Close Look at Some Auto Corrosion Problems" which begins on Page 14. This staff feature describes the changing atti-tude of both the automobile buyer and manufacturer, explains what is being done to alleviate corrosion and illustrates vividly the types of damage found commonly in many parts of the country. This survey of the prob-lem includes considerable data made available by both U.S. and foreign manufacturers. If you have an auto-mobile, you will want to read this feature.

WATER WELLS are known to suffer from the ravages inflicted indirectly by both aerobic and anaerobic bac-teria. Microphotographs of these organisms and some examples of typical corrosion damage encountered in water wells will be found in a two-page pictorial pres-entation on Pages 26-27.

MISSILES ENCASED in silos are expected to be ready to go on demand and without delay. The critical neces-sity for ultimate reliability in these weapons necessitates the best possible measures against corrosion damage to the hundreds of thousands of parts of which missiles are made. How some of the corrosion problems involved were solved is explained beginning on Page 28.

HOT WATER TANKS AGAIN! These appliances, constantly used in most homes in this country and be-coming increasingly common elsewhere, can benefit corrosionwise from design changes in the method of heating the water. Tests, conducted in public housing units in Ontario, also showed the deleterious effects of including copper piping in the system. Turn to Page 30.

STRESS CORROSION CRACKING of AISI Type 201 and Type 329 (Carpenter 7-Mo) deaerator trays in a feed water heater resulted from concentration of chlorides. Use of Type 430 is recommended as one solu-tion in an article beginning on Page 75.

NACE MEMBERS will have a prominent part in the First International Congress on Metallic Corrosion to be held April 10-15 in London. Of the speakers sched-uled to present papers, 21 are members of NACE. A plenary lecture also will be given by an NACE member. Titles of papers and NACE members concerned are listed in an article on Page 57.

NEUTRON IRRADIATION at flux levels of about 10^{12} nv at 400 C showed little effect on the oxidation characteristics of niobium. It is postulated that irradia-tion at this level was unlikely to change the oxidation rate. Turn to Page 77.

LIQUID FLUORINE AND LIQUID OXYGEN can be handled satisfactorily in most of the common metals. A study of these corrosives' reactions on a number of metals and non-metals is presented together with data on burning of metals and organic materials by com-pressive and tensile impact, friction, wear and other mechanisms. See Page 80.

STRESS CORROSION FAILURES cannot be elimi-nated by control of parameters established by experi-mentation and experience, an article beginning on Page 83 indicates. The problem can be minimized by proper design, changes in environment, reduction of effective stress or use of a protective layer.

CORROSION POTENTIAL of carbon steels is ma-terially affected by the amount of oxygen at the surface of the steel. For this reason a laboratory study of the effect of flow rate of sea water on the galvanic cor-rosion of different carbon steels was made. Turn to Page 89.

BILLIONS OF CANS make the subject of tin-plate performance an important one. A symposium of four papers, including one in two parts, considers several important aspects of the resistance of tin to foods. Per-sons concerned with the production of tin plate will be interested in this symposium, which begins on Page 93. The symposium was presented at a meeting of Ameri-can Chemical Society in Richmond, Va.

HIGH DENSITY POLYETHYLENE was used as a coating on 22 miles of 6⅝ inch pipe laid through highly corrosive coal field soil and swampland in Kentucky. The mill-coated pipe was welded in the field and joints were protected with pressure sensitive tape. Turn to Page 36 for case history.

NEW PRODUCTS of every kind known to interest corrosion workers are named and described and their manufacturers named in a classified list to be found in every issue of CORROSION. If you have not done so recently, you may find the information in this monthly feature useful. Because the items are classified alpha-betically, you save time by not having to read about things in which you have no interest. The editors of CORROSION scan tens of thousands of commercial press releases annually to sift out these items for your infor-mation.

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NACE Concept Justified, Current Activity Shows

WHEN A SMALL GROUP of pipeline engineers gathered in Houston in 1936 to discuss mutual problems, their primary aim was to exchange information. During the evolution of this group, which ultimately became the National Association of Corrosion Engineers, there gradually developed a broad view of the corrosion control problem which was the basis for today's NACE. This concept was that corrosion control information should be exchanged across industry lines for the mutual benefit of all.

NACE has developed since a better understanding of the implications of the corrosion control problem which now includes such unlikely extremes as bacteriology and atomic fission. It was further recognized by these pioneers that corrosion's ramifications required a system for bringing data from diverse sources to a focus so that they could be assimilated, classified and disseminated. These three functions, essentially, are those which NACE performs today. In addition (and it is hoped moreso in the future) some original investigations have been made into corrosion problems.

In the December 20, 1960 edition of the Wall Street Journal, a news story discusses the current efforts being made by industry to assimilate and screen the vast mass of information that presently is available. Among the statements was the following:

> "One result is that company after company has found itself duplicating research work that others already have done and fully chronicled."

This statement will have a familiar ring to NACE members. It is, essentially, the same observation that has been made time after time by those who have actively promoted the development of NACE. It is the basic reason for the existence of NACE. It is in seeking to prevent the waste implicit in the situation described that NACE has made its most valuable contributions to industry.

It has been said by those who are qualified to have an opinion, that there is perhaps a freer exchange of information among corrosion engineers than will be found among those working in other industrial areas. This free exchange has characterized NACE's activities from its inception, and, as far as can be determined now, will continue to be the association's outstanding asset.

There must have been a large measure of benefit by those exchanging the information for this free exchange to persist for more than 15 years. We think the benefits have been substantial for all who participate in NACE activities, and that they will be even more significant in the future.

In contrast to the practices of some other organizations, NACE has made available at modest cost to anyone concerned, whether or not he participates in the association's work, all of the valuable discoveries of its members. Its meetings at the local, regional and national level are open to all who care to attend; its publications are available to all.

This method of operation, while offering most to more companies with corrosion problems than almost any other that could be adopted, has its drawbacks. It is easy for any company to sit back and at a minimum cost, secure all the information NACE has to offer. It is easy for any company that elects to do so to take all and give nothing in return in the way of useful corrosion control information. Companies that have this attitude, however, should be glad that others are more appreciative, cooperative and understanding . . . otherwise there would be no benefits for them to absorb.

It is appropriate for NACE to take the opportunity at least once a year to express publicly its appreciation for the cooperation among companies and individuals that make its existence possible. It is especially appropriate to acknowledge with gratitude the support of the association's corporate members, whose help is invaluable in making it possible for NACE to progress.

If your company benefits from NACE's work, you may want to consider the benefits it may derive from joining the other corporate members of NACE and thus cooperate fully in the association's activities.

Abstract

Discusses corrosion damage and loss on automobile bodies in North America. Describes corrosion control measures that can be taken through use of more resistant materials, improvement of body design, protective coatings, treatment of environment (inhibitors for de-icing salts) and continued maintenance by car owner. Presents economic problems involved in using more resistant materials, problems of modern body styling that create box sections, hollows and crevices where corrosion can occur, and body undercoating to protect metal surfaces from corrosion.

8.9.2

CORROSION ATTACK such as this type can be caused by de-icing salts which are used widely in the northeastern United States to melt snow and ice from streets and highways. This 1954 model car photographed on a street in Cleveland, Ohio, had severe corrosion on the parking light enclosure. The bumper at the left also has been attacked and the body between the parking light and the bumper.

Five Methods Suggested

Automobile Body Corrosion Control Problems*

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PASSENGER CARS are scrapped at the rate of three million per year in North America. While most of these are scrapped because of damage from collisions or because they are obsolete, some reach the scrap heap because of corrosion attack. Those cars scrapped because of corrosion damage generally are corroded beyond economic repair.

Statistics show the average life of automobiles has been increased. Average life of cars scrapped in 1925 was six and a half years with an average mileage of about 25,000 miles. Average life of cars scrapped in 1951 was about 13½ years with mileage of about 120,000. This extended service life was due largely to improved mechanical components.

The older cars had no deep drawn body sections and were of less complicated construction than the automobile of the 1960's, but did have serious corrosion attacks along crevices formed at joints between bodies and fenders.

But modern car body design has created crevices, box sections and hollow areas where corrosion can proceed un-noticed by the car owner until perforations occur. Another stiff penalty derived from modern styling is that body sections are much more expensive to

For more information and photographs on automobile body corrosion, see Pages 14 through 24.

• Chromium trim corrosion
• Air pollution problems
• De-icing salt attack
• Body design problems
• Undercoating application
• Maintenance by owners

replace or repair because of their complex shapes. Use of the unitized body design with all parts welded requires the added expense of cutting and re-welding seams to replace most any body part.

Corrosion control on the modern automobile body can be achieved in the following five ways: (1) selection of more resistant materials, (2) improvement of body design, (3) protective coatings for metal surfaces subjected to corrosion, (4) treatment of the environment and (5) continued maintenance by the car owner.

Use of Corrosion Resistant Materials

To understand the problem of selecting the best corrosion resistant materials for use on automobiles, one should recall the fundamental mechanism by which metals are protected from corrosion. When chloride and sulfates are not present, corrosion of carbon steel in the atmosphere is negligible because of an adherent protective film of corrosion products on the steel surface. Resistance of these films is aided by the wetting and drying process of normal weather. Rain removes soluble corrosion products, making a more dense film. Intermitten drying by the sun tends to harden this film.

Unfortunately, steel which has good corrosion resistant characteristics in atmospheric exposures does not necessarily show good corrosion resistance when exposed

* Revision of a paper entitled "De-Icing Salts and Its Effect on Buried Structures and Autos" presented at the Toronto Section, National Association of Corrosion Engineers, October 13, 1960, Toronto, Canada.

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to sheltered corrosion conditions such as those found on the under side of automobiles and in the hollow areas of the body. Steels which would resist this sheltered corrosion are not used on autos because of high material costs.

A cyclical humidity accelerated corrosion test developed by one automobile manufacturer builds a corrosion product identical with that observed on specimens of underbody steel corroded in service.[1] This test machine produced the same corrosion damage to a specimen in 20 days as that recorded in three years on an atmospheric exposure rack at Bayonne, N. J. With this test, sheltered corrosion rates were found to be linear with time[2] and did not show the tapering off as on outdoor exposure racks. This test showed that alloying elements which produced protective rust formation outdoors do not necessarily contribute to protective rust formation under the conditions of sheltered corrosion. Some elements such as carbon which are reported to have little effect on the corrosion resistance of steels in outdoor tests seem to reduce corrosion under the sheltering environment produced in this test.

Tests also have shown that corrosion resistance is greater on steel which is allowed to dry periodically than on steel that is wet most of the time. Therefore, appropriate attention should be given in controlling automobile body corrosion by draining and ventilating critical surfaces.

Improvement of Body Design

The problem of drainage and ventilation for critical body surfaces is just one of many problems confronting the automobile body designer if corrosion control measures are to be considered in the design of automobiles.

No doubt the automobile design engineer is caught between the stylist and the production superintendents—thus required to design car bodies of the desired shape, stiffness and size at the smallest possible material and manufacturing cost. This imposed viewpoint has resulted in box sections, spot welded seams, rolled edges and other shortcuts to obtain the necessary combination of body rigidity and appearance.

Unfortunately, all these shortcut techniques produce dozens of sheltered locations on the car body at which corrosion attacks can occur.

For example, drain holes designed to remove moisture from the hollow spaces of the body often admit the corrosive they are designed to drain. Floor drains usually succeed in soaking the undercarpeting of the car's interior so that rapid corrosion soon perforates the floor sections which normally would have only superficial attack on the under side.

Drains that are provided in the body become plugged quickly. Locations of these drain plugs, obviously considered necessary or they would not be there, are not known to the car owner. He may hear water sloshing inside the car body and become inquisitive enough to find the plugged holes. Service manuals make no mention that these drain holes should be kept clear. The service station attendant or garage mechanic is rare who checks these drain holes when the car is on the grease rack.

The drain hole problem is an indication of the automotive industries' general viewpoint regarding corrosion control on

the car body. J. M. Callahan, engineering editor of "Automotive News," in a recent article stated that "underbody corrosion is merely a re-sale or aesthetic problem when the car's body is supported by a railroad track like frame." He also stated "that if this same amount of corrosion were permitted to eat away the underbody structural members of a unitized body, the results could be catastrophic. Serious structural defects would occur and eventual collapse of the whole car would not be an impossibility."[3]

Obviously, the automotive industry will design car bodies for corrosion control only when the structural elements of the car are apt to fail because of corrosion. This attitude is evident by the industry's current concern to provide corrosion protection for the new unitized body creations.

An example of the manufacturer being concerned over corrosion failure of structural body members is illustrated in the four-door hardtop models. General Motors used a zinc rich coating inside the rocker panels which supported the center door post on all four-door hardtops since 1955 but not on other contemporary models. Apparently, the prime consideration was for maintenance of strength, not appearance.

Use of Protective Coatings

The new unitized bodies have created new corrosion problems. Because body parts are welded, thus breaking down any protective coating on the metal be-

fore fabrication, auto manufacturers are trying new methods of corrosion control. Galvanized and aluminized steels are being used. Zinc rich coatings are being applied to specific areas.

A resume of the methods being used by some of the manufacturers to protect their new unitized car bodies is given below.

Chrysler

Each of Chrysler's unitized bodies is subjected to three metal cleaning baths, seven anti-corrosion dips, seven spraying operations and seven external paint operations. Essentially, this is the bonderizing process used by the auto industry, except that this process is accomplished by dipping the lower 18 inches of the body and spraying the upper portions. This is followed by dipping the lower 18 inches in a water base primer.

Rambler

Rambler's corrosion control process is unique in the industry in that the bodies are completely submerged in primer dip tanks. For additional protection to the inside surfaces of rocker panels, a long rifle-like paint gun is used to spray into the rockers a corrosion inhibiting, wax-like material

that does not dry. Instead of the alkyd type primer used previously, Ramblers are dipped in an epoxy primer pigmented with corrosion inhibiting iron oxide and zinc chromate.

Thunderbird and Lincoln

Underbody of the Lincoln, now in its third year with a unitized body, is protected against corrosion through the regular six-stage, sprayed-on bonderizing process plus dipping 18 inches of the body in a tank of water soluble primer. The Thunderbird body, built by Budd Company, receives the same corrosion protection as the Lincoln.

Ford Motor Company is using differentially coated galvanized steel in fabrication of the Falcon. About two-thirds of the hot zinc coating is wiped off one side of the sheet steel, and the heavier coating is formed on the inside of box sections. The more thinly coated outer surfaces receive a paint treatment for additional protection. This sheet is not used on the floor pan. Ford states that their tests show galvanized steel to be superior to coating systems tested in their labs.

Some of the corrosive problems on chromium and other bright trim work on auto bodies may be solved by reported improvements in plating techniques which would result in better corrosion resistance. This refers principally to the United States automotive industry—not to the automobile produced in Canada.

This matter can be clarified by a brief resume of plating practices in the two countries.

The United States was stockpiling nickel until quite recently. This nickel was not available to the automotive industry. The auto manufacturers' usual practice was to use a copper nickel chrome system with 0.0005 inch of copper with nickel to a thickness of 0.0015 inch. This was flashed with a minimum of about 10 millionths of an inch of chrome.

When the nickel shortage ended, the heavy investment in plating equipment for the old type plating could not be converted readily to a double nickel system. The U. S. industry is attempting to produce a two-layer nickel system which achieves only 0.0012-inch at best. Experiments also are being made with thicker chrome and thicker chrome systems that give thicknesses of 30 to 60 millionths. This is the bare minimum thickness for corrosion protection and requires special techniques such as modifications of chrome baths so that each chrome layer is produced with a different crack pattern to prevent alignment of cracks in the layers. Experiments also are being conducted on a crack-free chrome system with such innovations as pulsating chrome baths using a voltage variation in the plating bath to obtain thicker coatings in shorter times.

No nickel shortage has occurred in Canada. Since 1953, Canadian plated trim has been 0.0015 inch of nickel with a ten millionth of chrome. Anodized aluminum trim also has been used on some cars. Some cars have trim made of Type 430 chromium steel (16-18 percent chromium, ferritic).

Initial troubles experienced with Type 430, which showed loss of surface passivation when abraded, was due to insufficient pickling at the mill, forced on the mill operators by the auto trim manufacturers to lower buffing costs. At a

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considerable investment, suppliers of this steel are changing equipment to produce a bright anneal which will solve this problem.

Type 430 ferritic apparently will be the standard trim material for automobiles, excluding bumpers and die-cast grill work. Some Type 201 austenitic stainless (same as 18-8 with manganese instead of nickel) has been specified for autos recently but is slightly more expensive than Type 430.

Treatment of Environment

Some corrosion of auto bodies is caused by rain, calcium chloride dust treatments, abrasion, cinders, coal dust and other contaminants, but the greatest corrosion attack on cars is caused by de-icing salts used to melt snow and ice on streets and highways.

Two possible approaches can be made to treating this salt environment to control corrosion: (1) use of less corrosive materials as a substitute for salt if the substitute would not be too expensive and would do the job almost as efficiently as salt and (2) addition of chemicals to the de-icing salt to inhibit its corrosive attack on metal surfaces.

Alkaline salt mixtures have been suggested. Inhibitors have been used for many years in the refrigeration industry to inhibit cooling brines. Some of these additives could be used with de-icing salt. In 1947, the city of Akron, Ohio, used a 1 percent sodium di-chromate with satisfactory results.[4] Laboratory tests showed that a 2 percent mixture of di-chromate gave greater inhibition. This mixture was used in Akron as a standard for the winter of 1948-49. Although the di-chromates were suitable as corrosion inhibitors, they produced a bright yellow color on the snow and stained clothing. Also, this material is toxic, requires care in handling and can cause dermatitis on sensitive skin.

The same winter, glassy metaphosphates were used after tests showed this chemical to be equivalent to the di-chromates in inhibitor qualities. A green fluorescent dye was added so that even coverage could be obtained by visual means. This inhibitor is still being used satisfactorily.

The city of Rochester, N. Y., has

Technical Topics Included in Index

Technical Topics will be included in CORROSION's annual index published in the December issue. The Topics will be cross-referenced in the alphabetical subject and author index.

Persons who customarily extract Technical Section pages from each issue for binding are reminded that the Technical Topics pages should be extracted also for a more complete reference to technical information published in CORROSION.

conducted tests on its de-icing salt with a poly-phosphate inhibitor.[5] Data indicate that the city's corrosion rate was about 40 percent less than in cities using no inhibitor. Addition of an alkali phosphate to salt increased the penetrating power of the salt solution (probably decreased surface tension). These solutions penetrated joints and crevices in the automobile body and gave protection to these difficult to reach parts of the body.

Corrosion inhibitors added to de-icing salts are expensive. About 82,500 tons of salt were distributed on the streets of Metropolitan Toronto during the 1959-60 winter season. Total cost of inhibiting this quantity of salt would be about a quarter of a million dollars. However, automobile damage caused by salt corrosion has been estimated at $100 per year over the car's average life of 13 years. At this rate, corrosion losses on the 400,000 automobiles in Metropolitan Toronto would be forty million dollars. On the assumption that one-half of this loss could be prevented by use of inhibitors in road salt, an expenditure of a quarter of a million dollars would result in a saving of 20 million dollars to car owners of the city.

Maintenance by Car Owners

Continued maintenance of the car by the owner can help control corrosion damage. Mention has already been made of keeping drain holes clear in the body to prevent collection of water and other contaminants which can cause serious corrosion damage.

The car owner also can have his car undercoated to prevent underbody corrosion. Unfortunately, this coating often is sprayed over un-prepared surfaces, permitting the undercoating material to bridge cracks and crevices. Stone damage can penetrate this coating, allowing a corrosive poultice to form.

Sandblasted surfaces are probably the best for undercoating automobiles. However, it may be unwise to sandblast old cars because perforations may occur where previous corrosion damage has weakened a surface. Thus, only new cars should be sandblasted for undercoating.

Details and photographs of one company's undercoating system are given on Page 22 of the February, 1961, issue of CORROSION.

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American supermarkets serve 200 million customers each week and stock an average of 8000 items.

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One advantage of capitalism's free economy is shown in the price reduction of one flurocarbon resin which sells today at one-fifth its introductory price.

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Most of the 85,000 channel miles of the United State's television facilities are equipped for color transmission.

Staff Feature

Abstract

Discusses automobile body corrosion problems caused by complex shapes and configurations as evidenced by photographs presented of cars taken at random. Describes some corrosion problems experienced with chromium trim on cars, cooling system and exhaust system. Discusses trend of consumers to be more conscious of quality in products. Discusses measures taken by auto manufacturers to control corrosion. Air pollution and de-icing salt exposure problems are explained as two of a variety of exposures causing corrosion on autos. Describes in detail corrosion measures taken by two car manufacturers: Rolls-Royce and Volkswagen. Also outlines a commercial undercoating being applied to new cars by a Toronto, Canada, company to protect cars from de-icing salts. 8.9.2, 7.4.1, 4.2.1, 4.3.6, 5.3.2

Figure 1—Complex shapes and surfaces on underside of 1960 model American automobile illustrates difficulty of protecting this area from corrosion.

Modern Body Design Aggravates Damage

A Close Look at Some Auto C

CORROSION PROBLEMS of the American automobile have not been solved as evidenced by accompanying photographs taken in several areas of the United States and Canada. These corrosion attacks on the auto trim and body parts have occurred despite tests conducted by auto manufacturers to determine the corrosion resistant qualities of materials and engineering designs—all supplemented with detailed field observations recorded on IBM cards to tabulate what percentage of one-year-old cars was attacked by corrosion.[1]

Auto Body Corrosion Problems

Complexity of the corrosion problem to protect the American car's body parts is illustrated by the underside of a typical American auto shown in Figure 1. The many surfaces, sharp edges, curves, crevices, shelves and hollow spaces where moisture can be trapped or retained can become sites for corrosion cells to form, as shown in Figure 2.

Cross-section views of one 1961 model car's unitized body members (including the rocker panels beneath the doors) show that closed box sections have been created that will hold moisture, dust and other contaminants which can form moisture retaining poultices. (See Figure 3.) These poultices can be exceedingly destructive. Because these sections are neither ventilated nor exposed to sunlight so they can be dried out, they retain moisture; therefore the damage is much more extensive than it would be otherwise.

According to F. L. LaQue and E. J. Gergenroether,[2] the most significant factor in corrosion of automobile under-

bodies is that they have limited opportunity to dry out. The same also applies to the insides of doors or other relatively confined spaces in which moisture in warm air drawn in during the day will condense at night. This condensate plus rain that may leak in around window openings or be forced into crevices and hollow spaces by wheel splash obviously must be given an opportunity to drain immediately if corrosion is to be avoided.

Other automobile corrosion problems are illustrated in Figures 4 through 12, showing spots of corrosion on the exterior finish. None of these autos was more than two years old, but corrosion already had attacked the exterior surfaces. Rough welded areas, drainage troughs clogged with weld and filler material and troughs formed along horizontal chrome trim (especially over the front windshield) also are excellent sites for corrosion to begin even on new cars, as shown in Figures 4-7.

Although a walk through a parking lot or along any street in most areas reveals cars with varying degrees of body corrosion as seen in Figures 4-12, auto manufacturers have taken many steps to combat the corrosion problem. Materials with proven corrosion resistance are being used where economically feasible, coatings are being applied for added corrosion resistance and design factors are being considered to eliminate areas where moisture and dirt can be trapped.

Corrosion on Chrome Trim

Corrosion from poultices trapped inside box section frame members and other hollow parts of the body does not become apparent as quickly as does rust

on the auto's chromium trim.

Some engineers believe that the unfavorable corrosion resistance that has been experienced with chromium parts on cars is the result of insufficient test methods and standards.[3]

An example of one auto company's efforts to test its bright work for resistance to corrosion is the three tests used by Volkswagen to determine corrosion resistance qualities of hub caps, bumpers and other chrome parts.[3] The first corrosion test is in an artificial industrial atmosphere using controlled conditions to expose the parts to condensation, sulfur dioxide and carbon dioxide. The second, a shortened test, was devised to check corrosion resistance of samples from each day's production of chrome parts. This test is designed primarily to indicate the porosity of the protective layers of the chrome. The third test is

Figure 2—Crevices, shelves and varied shaped surfaces on a new model compact American auto.

conducted in open air to check how valid the other two tests have been in practical application. These weathering tests, however, have the disadvantage that their results can never be taken as a norm because climates vary so much.[3]

According to Volkswagen engineers, a new type chromium plating bath has been developed to produce refined chromium layers two microns thick. (0.000078 inch) without cracks. Previous plating baths produced porous chromium layers with cracks that permitted moisture to corrode the nickel layer used as the corrosion protection layer in most chrome trim parts. The chrome layer is used primarily to give a polished finish.[3]

Many engineers in the chemical, metal and galvanizing industries agree that more test and research work needs to be done on chromium plating to achieve more corrosion resistant trim work for the automobile.[3]

A recent survey made by the magazine "Materials in Design Engineering" showed two-thirds of the readers were dissatisfied with the chromium on today's cars. The survey indicated that

has been done, for example, to eliminate rust and scale from the car's cooling system.[6-9] Inhibitors have been developed and evaluated to help solve radiator and engine corrosion problems in water cooling systems.

Aluminum engine blocks used on 1960 and 1961 models have created new corrosion problems in the cooling system. Because these engines are not wholly of aluminum, galvanic corrosion can occur between the dissimilar metals if the engine is liquid cooled. Aluminum is too soft for use as cylinder walls; thus cast iron sleeves are inserted to sustain piston wear. Design engineers of the new water-cooled aluminum engines on the 1961 Rambler, Oldsmobile and Buick compacts, for instance, claim to have eliminated this undesirable galvanic couple.[10] (Pontiac's Tempest and Chrysler Corporation's Plymouth, Dart and Lancer have optional aluminum engines.)

Photographic examples of this type galvanic corrosion attack in an engine are shown in Figure 13. These cast aluminum manifolds were bolted to cast iron cylinder heads, setting up a galvanic

to Corrosion Problems

even in areas where de-icing salts are not used, chromium plating on automobiles is not performing adequately.[4]

Furthermore, information concerning recent nickel shortage problems affecting chromium trim parts on American cars has just been published.[5]

Cooling System Corrosion

The body and chrome parts, however, do not produce all the corrosion problems on the automobile. Extensive work

coupling that caused pitting and leakage failures on water ports numbered one and six. An oil soluble inhibitor was used to solve this problem so that satisfactory service life could be obtained from the engines without extensive overhauling and replacement of parts.[11]

Exhaust System Corrosion

The tail pipe being dragged beneath the car and the loud engine roar are dramatic results of exhaust and muffler systems gutted by corrosion attack. This corrosion damage is probably of more immediate economic concern to automobile owners than damage to body parts.

It is estimated that 11 million replacement mufflers for passenger cars alone were manufactured in 1959.[12] These mufflers were replaced primarily because of corrosion damage and at an estimated wholesale cost of $270 million.[13]

Muffler manufacturers are using numerous methods in their attempts to solve this costly corrosion problem. A ceramic coated muffler is one attempt. Another is a special design to eliminate moisture traps inside the muffler. Still another attempt is the use of special

Figure 3—Cross-section views taken from a catalog on a 1961 model American compact car illustrate the closed box sections on the unitized body in which moisture, dust and other contaminants can be collected to form highly destructive corrosion poultices.

Figure 4—Corrosion along windshield on 1959 sedan. Figure 5—V-shaped trough fin on 1959 car had corrosion in bottom of trough where dirt and other foreign matter had collected. Dark area shows large spot where paint had been undercut by corrosion. Figure 6—Rough weld on rear window of 1959 station wagon showed beginnings of corrosion where moisture was trapped. Figure 7—Flat area between rear window and trunk lid on this 1959 car had corrosion along the welded seam.
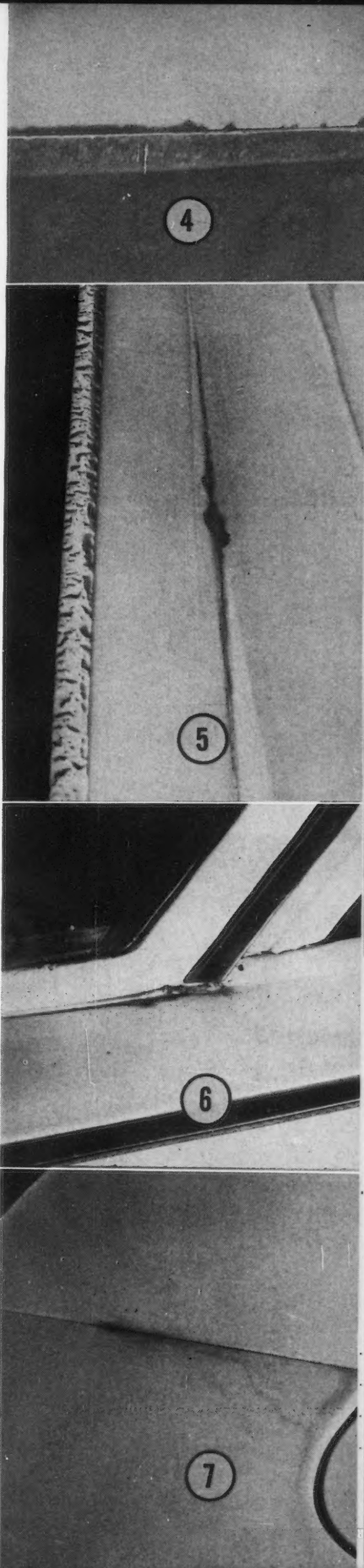
Modern Body Design—

alloy metals to resist the corrosive acids formed in the exhaust system.

A detailed survey of these diverse methods to control auto muffler corrosion is scheduled for publication in in a future issue of CORROSION. This feature will describe various muffler designs, materials selected for heat and corrosion resistance, coating and alloy materials as well as some corrosion tests conducted by muffler manufacturers.

Quality Conscious Consumers

Although corrosion attack on body parts (and even the muffler) does not adversely affect performance of the car's mechanical parts, this corrosion problem is becoming more important because consumers are becoming more interested in quality and because corrosion can affect the safety and performance of unitized

Figure 8—Severe corrosion under the roof overhang on this 1959 station wagon on the right side; Figure 9 shows the left side of the car. Figure 10 shows the top view of the overhang in Figure 9, where filler material and rough welds had formed pockets in which dirt collected. (Owner of this car stated the car is washed each week by attendants where the car is stored each work day. Figure 11 shows corrosion along a welded seam on another 1959 car. Figure 12 illustrates corrosion that can occur where unitized bodies have rough welds and where chromium trim overlaps these rough welds. This is another 1959 car. (All cars in Figures 4-12 were photographed at random in Houston, Texas.)

car bodies.[14] Some manufacturers are convinced that so-called "planned obsolescence" has gone too far and that money for annual model changes could be spent to better advantage on improved product quality.[15]

A possible trend toward reducing outlay for model changes so that funds can be expended on improvements was indicated last fall by American Motor Company's statement that no more annual model changes would be made in its Rambler American cars.[16]

Another trend indicating improved quality in autos was recent newspaper announcements by Ford, General Motors and Chrysler that warranties on their 1961 models have been extended to 12 months or 12,000 miles—a substantial extension over the previous warranty on parts for 4000 miles or 90 days. Ford extended its warranty on the 1961 Lincoln to two years or 24,000 miles.

These extended warranties on mechanical parts and the increased service life of the American automobile[5] have resulted largely from improved mechanical parts. As a probable result of these improvements and of the increasing number of two-and three-car American families, trade-ins may become less frequent. Thus, more attention should be given to corrosion control of the auto body to extend its service life and to retain its showroom attractiveness to parallel the extended life of the mechanical parts.

A survey of promotional literature obtained at auto dealer showrooms indicates that the Detroit manufacturers have foreseen the consumer's probable

Figure 13—Advanced galvanic corrosion of cast aluminum water outlet bolted to cast iron cylinder head. Corrosion in ports number one and six caused water leaks through the bolt holes.
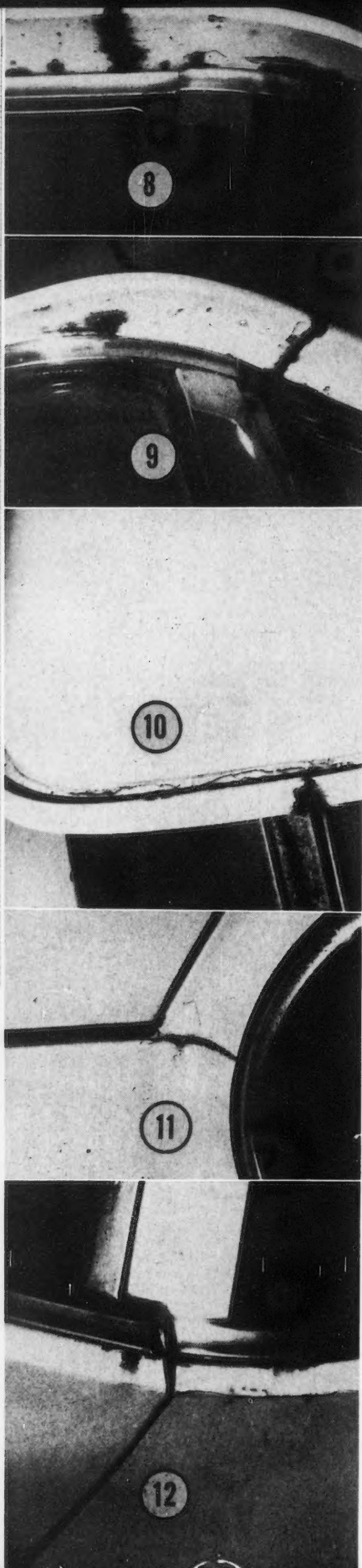
concern over auto body corrosion. "Rust-proof" unitized bodies are mentioned in brochures obtained on the Oldsmobile F-85, Rambler, Plymouth, Valiant, Chrysler, Mercury, Lancer, Ford and Thunderbird. Brochures on the Lincoln Continental, Thunderbird, Falcon, Comet and Ford cars mention the use of galvanized steel for structural body members including the important rocker panels under the doors.

In brochures obtained on the Buick, Imperial and Chevrolet, no mention was found on corrosion control measures to protect the auto body parts.

A survey across America of the 1961 cars after one to two years' service will be worthwhile to determine the long-term effectiveness of the "seven step rust-proofing," dipping, spraying, use of galvanized steel and other measures claimed for these cars as means to control corrosion.

Variety of Exposure Involved

Because of the wide variety of climatic exposures to which the American car can be subjected, elimination of auto body corrosion problems is not simple. In some regions, cars are exposed each winter to the severe attack of de-icing salts used on streets and highways. Other cars are operated in areas suffering from heavily polluted air.

Air Pollution Problems

Pollutants that can corrode body parts may vary from one city to the next. And even accidental exposures that could occur in any city as described below can create corrosion damage.

For example, cars parked near a grinding operation had to be repainted because brown stains occurred where iron particles fell on the auto surfaces and attached themselves tenaciously to the paint. Mechanism of this staining was postulated to be formation of ferrous hydroxide in the presence of moisture. Being in a colloidal form, the hydroxide diffused into the paint film. After drying and oxidizing, a brown stain of ferric oxide remained.[15]

Other examples of corrosion damage to auto finishes by air-borne particles include some cars in Detroit, Mich., that required repainting after mortar dust from nearby brick building demolition operations settled on the cars and combined with moisture to cause corrosion damage. This damage, which appeared to be crazing, can be reproduced by sprinkling mortar dust on paint test panels and covering the panel with a moist blotter.[17]

Figure 14—Examples of corrosion attack caused by de-icing salts. Cars A and B suffered corrosion attack where salt and other contaminants were retained in a shelf along the inside of the rear fenders. These two cars were photographed in Cleveland, Ohio. Car C, photographed in New York City, has corrosion along the chromium trim, causing the paint film to be undercut and to peel. Car C has suffered complete perforation above the headlight where wheel splash has forced de-icing salts into a hollow, confined space. This car was photographed in Columbus, Ohio. Car E, a 1958 model photographed in Cleveland, has severe pitting along the trunk lid, evidently where moisture has been entrapped in the hollow box section designed to reinforce the lid. Car F has complete perforation below the trunk lid and corrosion on the bumper. Car G, photographed in Columbus, Ohio, has suffered perforation on the body panel behind the front wheel and along the rocker panel below the door.

De-Icing Salt Problem

The devastating corrosion attack on car bodies caused by de-icing salts used to melt snow and ice during the winter months as illustrated in Figure 14 is another of the varied exposures to which a car can be subjected. The cars in the figure were photographed in cities where de-icing salts are used. These illustrate the fast penetration which can occur when salt water is

trapped in the hollow spaces, shelves and enclosed areas of the car body, as shown on the 1958 model. Wheel splash forced the salt water and other contaminants into the area above the auto headlight shown in Figure 14D. Complete perforation resulted.

Automobiles operated in cities using de-icing salts have suffered more corrosion than autos in cities not using de-icing salts, according to a five-year survey made by General Motors.[18] In Detroit, where salt is used, 58 percent of the one-year-old cars examined showed corrosion along chrome mouldings. No other body area was checked in this survey. Only 35 percent of the same-year model examined in Miami (where no salt is used) showed corrosion along the chrome mouldings. This comparison is more significant when one realizes Miami has twice the annual rainfall and much higher relative humidity than Detroit.[18]

Extent of this particular corrosion problem on the automobile can be understood more easily from an estimate that each car in Toronto, Canada, suffers an average $100 corrosion damage per pear because of de-icing salts.[5] That city distributed about 82,500 tons of salts on its streets during the 1959-60 winter. Buffalo, N. Y., used an estimated 23,000 tons of de-icing salts during the same winter season.[19]

Corrosion Control Methods Used

Manufacturers' efforts to protect automobile body parts from corrosion include use of galvanized metal, zinc coat-
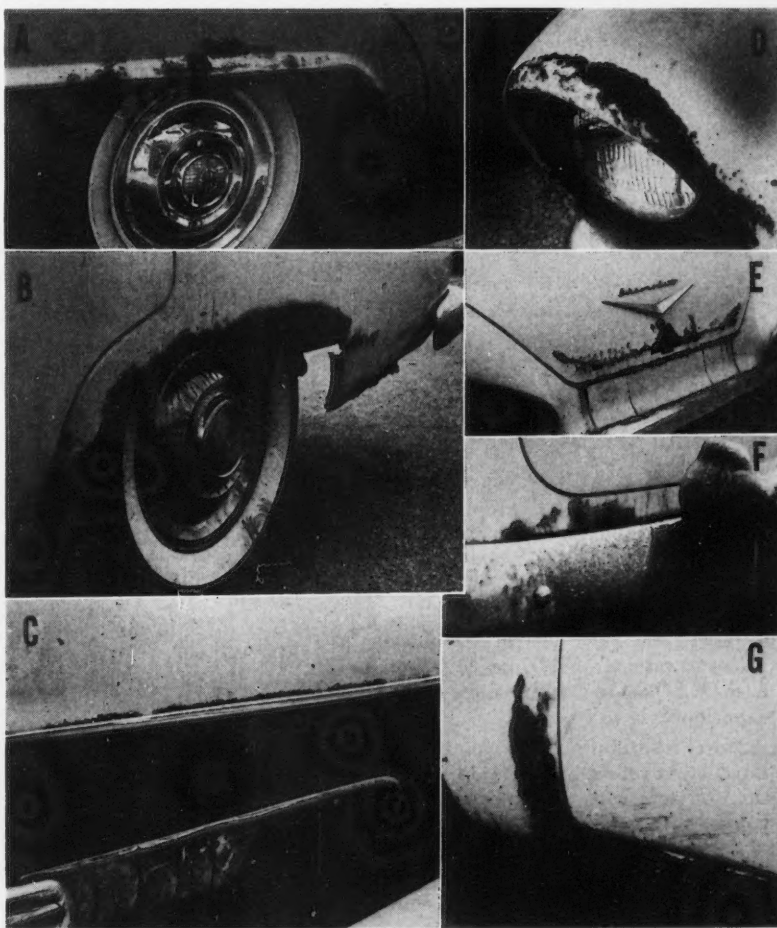
Volkswagen Tests Each Paint Charge

Modern Body Design—

(Continued From Page 17)

ings and phosphatizing processes. Most of the 1961 models' so-called "rustproofing" involves a protective coating that is applied by dipping or spraying. A typical dipping operation or coating a unitized body is shown in Figure 15.

The importance placed on good protective coatings for automobiles is indicated by the tests conducted by Volkswagen. Three laboratory tests are conducted before release of each paint charge, supplemented by outdoor exposure tests at several sites throughout the world.[20]

First of the three lab tests is for economy and spreading rate of the paint in which viscosity, specific gravity and hiding power are determined. In the second test, physical characteristics of the paint charge are checked, including color, gloss, uniformity, consistency, fineness of grind, hardness and abrasion resistance. The third test is made to check the paint's durability—an accelerated laboratory test in which weathering resistance, adhesion, flexibility, impact resistance, and light fastness are determined.[20]

In this third test, coating adhesion is checked on artificially aged paint samples by cutting through the coating to the bare metal. Then the test panel is bent through an 180-degree arc over a 0.2-inch mandrel. There must be no loss of adhesion to meet specifications.[20]

Flexibility and impact resistance of the paint are checked in this third test by a device that subjects the test panel to an impact equivalent to flying stones that might hit the car's painted surfaces in highway service. Specifications stipulate that there must be no cracking or flaking of the finish in this test.[20]

Although not a fair comparison with American autos because of price differences, the coating systems used on Rolls-Royce automobiles are indicative of what one manufacturer considers necessary for long service life of a car's body. The steel shell and aluminum body parts on the Rolls-Royce are phosphortized and given an acid etch pre-treatment primer before two to five coats of synthetic primer surfacer are applied, followed by five to nine coats of color paint.[21]

Other corrosion control measures on the expensive Rolls include the following: (1) coating of all metal-to-metal surfaces with zinc filled primers and sealers on spot welds, (2) interior box sections constructed of zinc plated steel, (3) underside coated with ½-inch thick bituminous emulsion, (4) nuts, bolts and washers of cadmium, chrome, nickel or zinc plate, (5) exterior fittings of stainless steel or steel plated with copper, nickel and heavy chrome.[21] Even the tail pipe is chromed.[22]

Still another corrosion control measure on the Rolls-Royce is the practice of vacuum sealing the box section frame to keep moisture out.[23]

New auto body designs which permit simplification of the undersides may become a more commonly used method to eliminate the cracks, crevices, hollow spaces and box sections which create areas for corrosion cells to form. Chevrolet's Corvair has a rear-mounted engine and Pontiac's Tempest has its transmission in the rear—both indicative of new body designs that could permit simplification of the underside to help eliminate the many complex areas where corrosion can attack.

The complicated underside of the American car in Figure 1 is contrasted with the simple underside of the German Volkswagen shown in Figure 16. Because of this simplified floor pan construction, the Volkswagen is easily undercoated by the manufacturer for protection from corrosion. This floor pan is sealed with rubber to make it practically air tight. Volkswagen has received reports that the car will float with little water seeping into the passenger compartment though the manufacturer does not recommend the car for this type service.[3]

Career opportunities in corrosion research

*   *   *
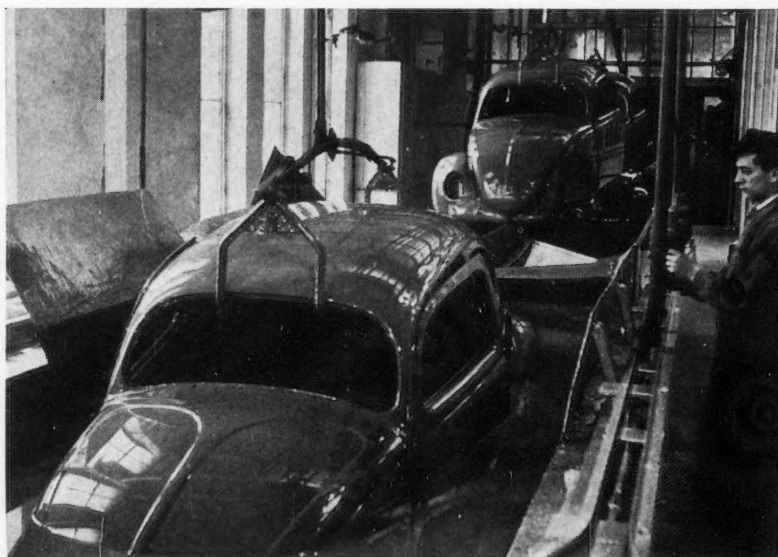
Figure 15—Typical dipping operation used to coat unitized bodies. Most American manufacturers use this type protection.

Dow division uses X-TRU-COAT for a 30-mile run through swampy Louisiana soils

Dow Chemical Company's Louisiana Division selected 4½" O.D. X-TRU-COAT (Republic's *plastic-coated* line pipe) for a service installation involving long runs through swampy soils near Plaquemine, Louisiana.

A 30-mile pipe line was needed to transfer products between Dow's Plaquemine facility and storage points. Dow specified X-TRU-COAT on the basis of corrosion-resistance, ease of installation, and overall cost comparisons.

The high density polyethylene coating of Republic X-TRU-COAT is continuously extruded over "live" undercoating to seal out electrolytic action. X-TRU-COAT is immune to ground chemi-

cals and resists shipping, stringing, and backfilling damage.

X-TRU-COAT Plastic-Coated Line Pipe (Republic coats it at the pipe mill) is available in 1.050" through 8.625" O.D. You can also have the coating on Republic Light Wall—in 1" through 4" nominal—for gathering and distribution systems.

The complete package includes Republic X-TRU-COAT, X-TRU-TAPE Joint Wrap, and X-TRU-PRIMER. For information or quotations, call your nearest Republic representative or mail the coupon. X-TRU-COAT is produced under the Dekoron® Process.

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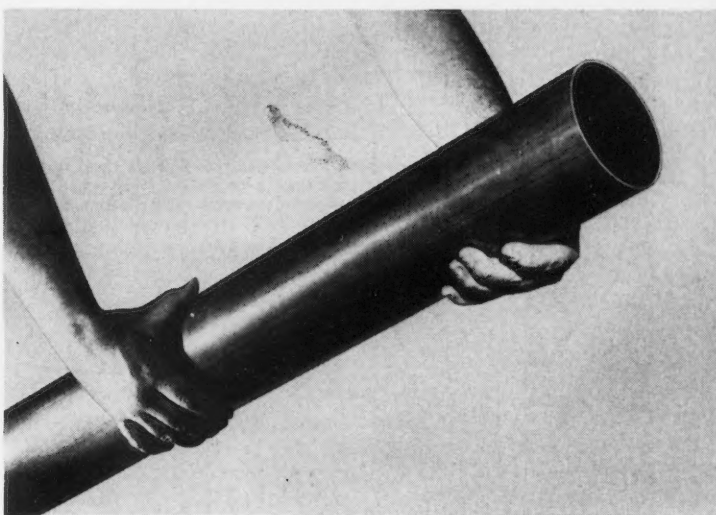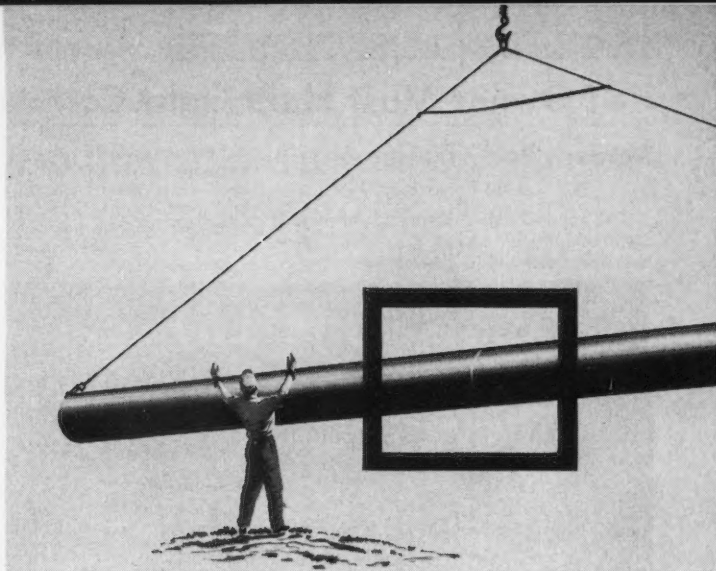
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Company_____

Address_____

City_____Zone____State_____

Owner Must Help Fight Corrosion

Modern Body Design—

(Continued From Page 18)

The manufacturer does not have full responsibility for corrosion control measures on automobiles. The car owner also must properly maintain the vehicle so that control measures used by the manufacturer will give long service life.

Frequent washings generally are recommended in the owner's manual for each new car. Despite advertisements and promotional brochures which suggest that no waxing is necessary on the new acrylic finishes, most auto manufacturers suggest in the car owner's manual that the finish be given proper cleaning and occasional waxing if the original luster is to be preserved.[25]
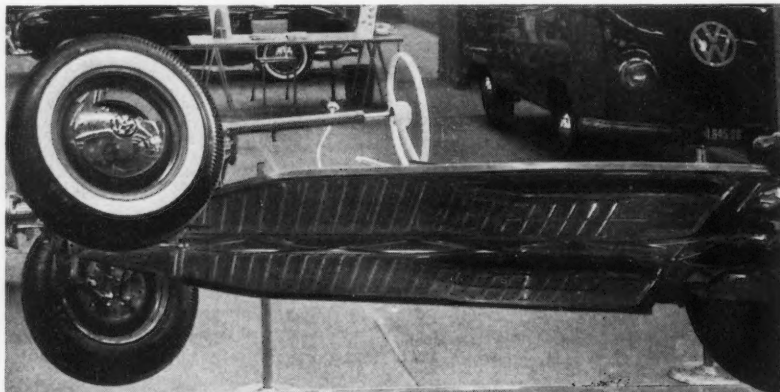
Figure 16—Underside of German-made Volkswagen shows simple floor pan which is sealed and rubber coated by the manufacturer for corrosion prevention. This simple pan contrasts sharply with the complex underside of American automobiles illustrated in Figure 1.
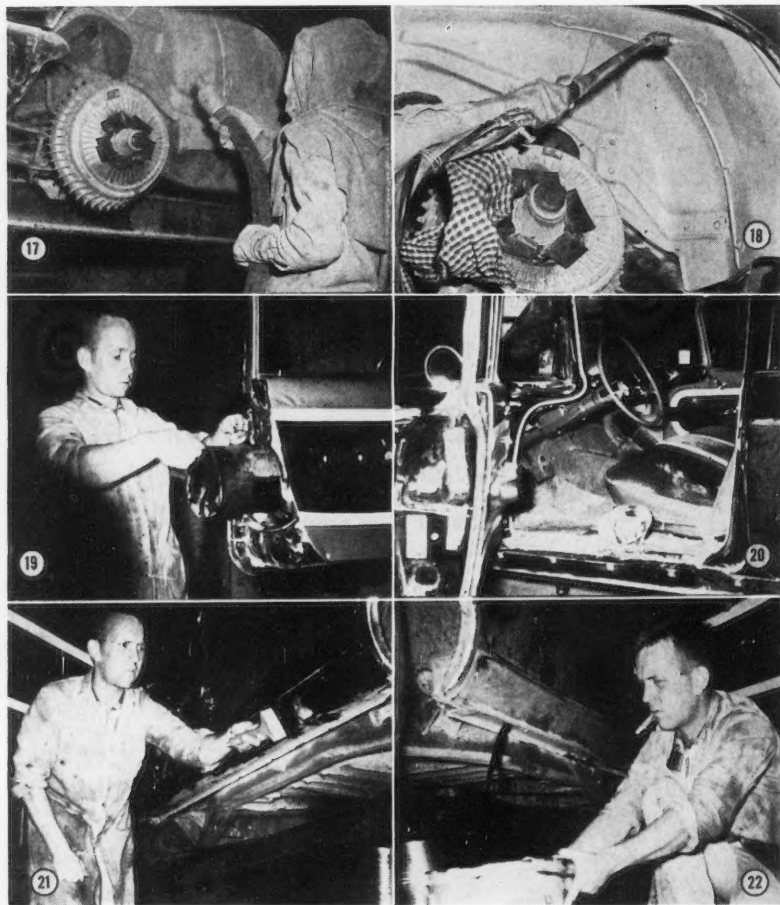
Conclusion

Although some measures are being taken to control corrosion on the American automobile, quality-conscious consumers soon may be demanding that further protection be provided and that a logical engineering objective be achieved to make body components last as long as the auto's mechanical parts.

Principal corrosion problems on the car body involve crevices, shelves, pockets, closed-in boxes and other areas where moisture can be entrapped by poultices formed by dust, mud, salt and other contaminants. Complexities of shapes and formations on both the car's underside and its painted exterior also have created areas of potential corrosion attack. Frequent washings as recommended in the car owner's manual and proper waxing seemingly have failed to

eliminate all the corrosion attacks on exterior surfaces as evidenced by Figures 23-28. And undercoating (at additional cost to the owner) seems to be only a partial answer to the car's underbody corrosion problems.

As corrosion and coatings engineers have learned from long experience, a coating's performance is improved greatly if the surface to be covered has a simple profile with no sharp edges, crevices, projections, curved sections with a short radius and box sections reduced to a minimum.

The car owner also needs to be adequately informed about maintenance steps he should take to protect his car from corrosion attack. For example, no mention is made in owners' manuals of the presence of drain holes and plugs on the car's underside or of the necessity for keeping these holes open to drain entrapped moisture from body sections.[5]

Figure 17—After dirt, grease and other deposits are scraped from the underside of the car, the under-fender areas are sandblasted to gray metal. Then the surfaces are spray coated (Figure 18). Figure 19 shows coating being poured into the bottom of a door which has been dried by hot air blasting. Coating material is drained out the bottom of the door, leaving the area coated inside. Figure 20 shows the funnel used to pour coating material inside the rocker panel. Surplus coating material is later drained, as shown in Figure 22. Figure 21 shows a protective coating being applied to the outside surface of the rocker panel. (Figures 17 and 18 courtesy Toronto Star Syndicate.)

Modern Body Design –

In Australia, a Volkswagen auto became the first "boat" to float under a bridge during special opening ceremonies. Although staged as a publicity gag, the incident proves the desirable watertight qualities of the closed floor pan construction. The engine of the car was modified to provide a snorkel on the carburetor intake and an exhaust extension. Aquatic power was provided by a propeller driven by a shaft through the rear bumper.[3]

The average American car buyer will not be interested in having a car with a smooth, simple and easily coated floor pan so that he can float his car across streams and rivers, but he will be interested in the assurance that such a floor pan could eliminate hollow pockets and crevices and could enclose control wires, cables and other parts for protection from wheel splash and subsequent corrosion attack. He will also be interested in eliminating water-soaked floor carpeting or covering in his automobile, a common problem among American car owners.

Special Undercoating Application

To help eliminate possible corrosion attack on the complicated underside of the American automobile, especially from the severe attack of de-icing salts, a Toronto, Canada, firm recently has established a special coating service to undercoat new cars.[24] Some of the steps in this coating system are shown in Figures 17 through 22. This system includes under-fender areas, seams, rocker panels, underside of chrome surfaces, floor and trunk wells and bottoms of doors. Cost of this coating service for American compact cars is $55, $65 for standard American cars and $75 for large cars such as Cadillac and Lincoln.[24]

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Figure 23—Ornamental spare tire fixture on 1959 car's trunk lid permits moisture to be held, causing possible corrosion next to chrome trim. Figure 24—Cracks and complete perforation have occurred below the trunk lid on this 1956 convertible. The metal was so corroded that the photographer accidently punched his finger through this area. Figure 25 shows the corroded chrome around the tail lights on a 1958 car. The chrome on the other side of the car was in excellent condition. Figure 26—Severe corrosion along bottom of tail gate on 1959 station wagon. Figure 27—Corroded area on top of 1960 automobile. An indented area was designed in the car's roof where moisture can be held when the car is not in motion. The small pool of water shown has corroded through the paint film. Figure 28—This V-shaped tail fin on a 1959 car (same as Figure 5) has corrosion along the chrome tail light with a deep pit at the top. (Cars in Figures 23 through 28 were photographed at random in Houston.)

Corrosion Attack in Water Wells*

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Layne & Bowler, Inc.
Memphis, Tennessee

MOST of the common iron and sulfur bacteria contribute to the corrosion process experienced in water wells. Iron precipitated by the iron bacterial may form tubercles with an anaerobic area in the center. Differential concentration cells are produced which cause direct corrosion or may be further aggravated by possible growth of anaerobic bacterial in the area.

Sulfur bacteria create strongly acidic conditions, thus creating a vigorous source of corrosion. Aerobic sulfur bacterial can oxidize sulfur or reduce sulfur compounds to sulfuric acid to promote acid corrosion.

These bacteria can reduce the flow of water into the well and must be removed periodically with acids and strong chlorine solutions.

FIGURE 1—Leptothrix aerobic iron bacteria. At first, elements of cylindrical cells within sheath are thin and colorless. Later encrusted with ferrous hydroxide, cells become thicker and yellow or brown in color. FIGURE 2—Gallionella aerobic iron bacteria. When encrusted with a deposition of iron, filaments resemble a row of beads. Under active conditions, these grow into mass as thick as one-inch in about two weeks. FIGURE 3—Crenothrix aerobic iron bacteria. Sheaths are thin and colorless at tip; thick and encrusted with iron at base. Organisms are found in stagnant and running water containing organic material and iron salts. FIGURE 4—Sphaerotilus aerobic iron bacteria are found most abundant

*Extracted from a paper titled "Some Corrosion Problems in Water Wells" presented at a meeting of the Sabine-Neches Section, National Association of Corrosion Engineers, January 28, 1960.

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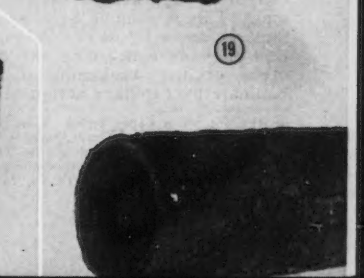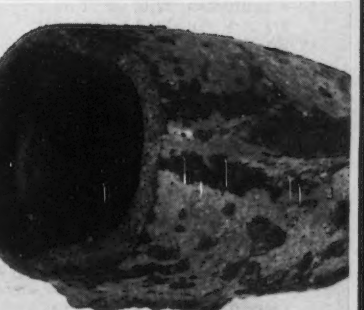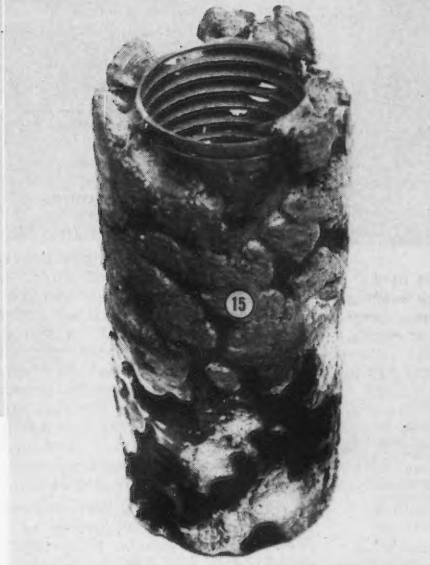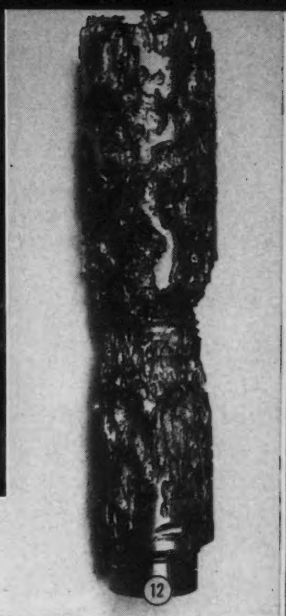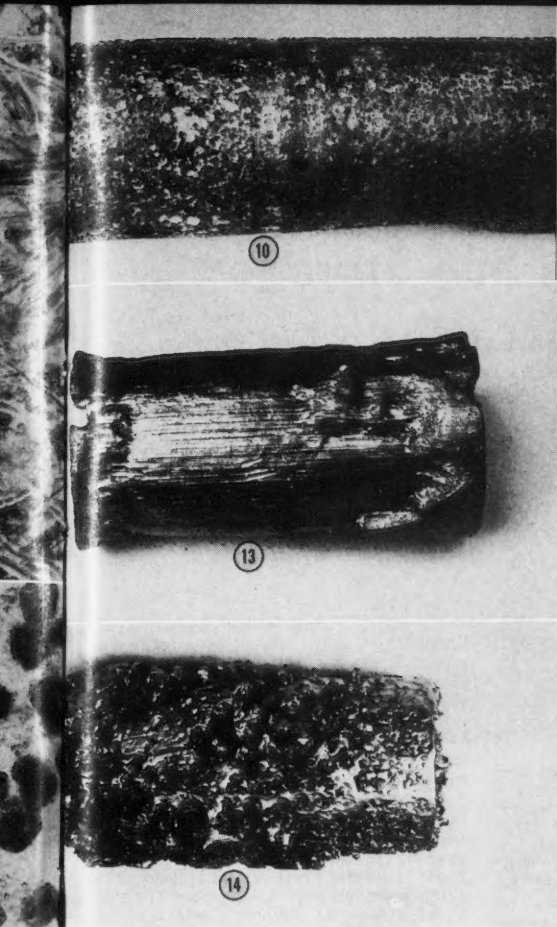
in waters of inferior organic purity, especially when stagnant. The growth appears as a soft, slimy, grayish-brown mass. FIGURE 5—Clonothrix aerobic iron bacteria closely resemble Sphaerotilus in Figure 4, but sheaths are encrusted with iron or manganese. FIGURE 6—Siperocapsa aerobic iron bacteria, found most often in exposed ground reservoirs. Cells are spherical or oval with one or more embedded in a mass of capsular material surrounded by ferrous hydroxide. FIGURE 7—Sulfur bacteria of many varieties usually are found in water containing hydrogen sulfide. One type decomposes sulfide, storing up sulfur in the free state, and afterwards other bacteria oxidize it to sulfates. Iron bacteria generally cannot exist under conditions favorable to sulfur bacteria. FIGURE 8—Bronze pump impeller suffered cavitation, leaching of copper from bronze and general corrosion and erosion from operation in acidic water containing excessive chlorides, sulfates and total solids. FIGURE 9—Steel oil tubing used in water well to house pump shaft had differential aeration corrosion attack at rubber bushings on the combination coupling of the column pipe. Some cavitation and pitting attack also is visible, caused by high carbon dioxide in water. FIGURE 10—Pitting attack on Monel shaft sleeve of water lubricated pump resulted from hydrogen sulfide in water. Sleeve was chisel cut lengthwise for removal from shaft. FIGURE 11—Crevice corrosion attack on chome stainless steel shaft threading resulted from 125-day laboratory rotation and static tests in synthetic sea water. FIGURE 12—Cavitation, impingement and crevice corrosion on chrome stainless steel shaft coupling were caused by excessive water velocity, caused by use of a column pipe too small in diameter. Water had high chloride content. FIGURE 13— Hydrogen sulfide corrosion, abrasive erosion from solids and high velocity cavitation attacked carbon steel shaft coupling. Grain lines show effect of hardening cold-rolled steel shafting from which coupling was machined. FIGURE 14—Carbon steel shaft coupling from water lubricated pump was attacked by aerated, high chloride waters containing carbon dioxide and high total solids. FIGURE 15—After 10 years in water lubricated pump, this carbon steel shaft coupling suffered high hydrogen sulfide attack, accelerated by cavitation. FIGURE 16—Corrosion attack on coupling was attributed to velocity effects, high carbon dioxide in water and possibly some electrolysis because shaft had little attack. FIGURE 17—Pitting and tuberculation in steel eductor pipe were caused by water containing hydrogen sulfide and carbon dioxide. Pipes were not properly butted on assembly in conmbination coupling. FIGURE 18—Aerated, high carbon dioxide water caused impingement attack on steel flange nut. Water fell from exposed well screen. FIGURE 19—Cast iron combination coupling (small diameter) and carbon steel shaft coupling were attacked by erosion, corrosion and graphitization.

Some Corrosion Problems of Missiles in Silo Storage*

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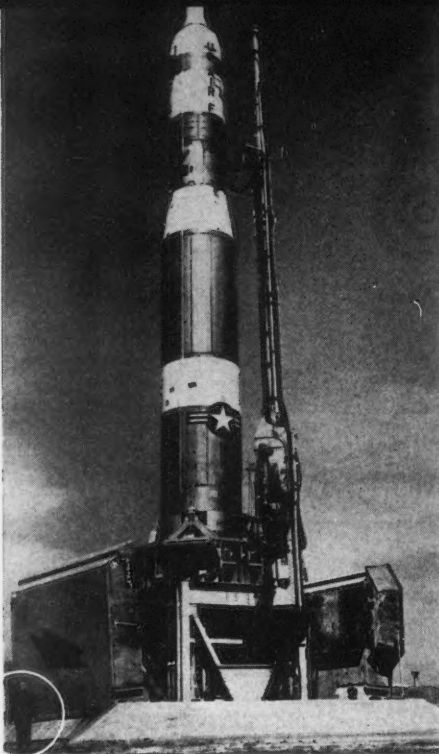
Figure 1—Titan missile elevated from its storage silo, ready for launching. Service boom is used to complete fueling for launching. Cover doors to silo are shown on each side of missile.

Abstract

Explains corrosion problems that may be encountered in long term storage of missiles in underground silos. Discusses problems in controlling atmosphere inside the silo and the missile to prevent corrosion, corrosion control measures used and techniques used to measure corrosion. Detecting systems covered are visual and electrical methods.   7.1

COMBAT-READY missiles stored in concealed, underground emplacements is a strategic concept for implementing the United States defense policy of striking back after an enemy attack. Any weapons system, therefore, must be protected from external destruction.

Liquid fueled rockets, such as Titan, and solid propellant missiles, such as Minuteman, will be stored in silos in a state of constant alert, with only go-no-go checkout and fuel top-off to be completed prior to launching. Silos and their control points will be constructed to withstand anything but a direct hit of a nuclear warhead.

The missile must be preserved in the excavation environment. Regardless of the time in storage, the weapon must remain substantially invulnerable to corrosion which can render a missile inoperative as effectively as a direct bomb hit.

For purposes of this article, corrosion is defined as any type of deterioration caused or aggravated by the environment. This is a much broader definition than is normally used. Whether mention is made concerning the rusting of metal or the weakening of a plastic laminate by capillary action of moisture

following the exposed glass thread, all such reactions of the missile to its environment are defined broadly in this article as corrosion.

From the moment a missile is placed in an environmentally unprotected silo, deterioration commences. Missile reliability declines as deterioration progresses. Environment within the silo must be controlled to the degree that obviates this aging process. Sources of the deterioration must be determined in advance, remedial measures sought and action taken to anticipate and correct through environmental control.

Moisture Intrusion Into Silo

Normal sealing will not prevent the entry of water. The silo cover will require a watertight seal to prevent entry of rain water and melting snow. The problem is aggravated by amounts of alkalies leached by water from the soil. Acid type infiltrations also would be undesirable. Even small amounts of water accumulated in the silo can cause eventual breakdown of the dehumidifying system. Corrosion, of course, will start promptly. Table I presents a list of corrosive agents found in rain water.

Probable Natural Silo Environments

Underground envelopes 80 to 100 feet deep typically show temperatures approximately equal to the yearly average air temperature at the surface. High relative humidities and cyclic condensation of moisture occur at depths affected by the above-ground temperatures. Temperatures from the surface down to approximately 35 feet will average the mean annual temperature at a given site. For the United States generally, this will vary between 40 and 70 F.

Relative humidity at the silo bottom probably will exceed 90 percent without air conditioning. An average relative humidity of 86 percent in underground mines between 50 to 400 feet deep has been reported by the Bureau of Mines. Thus, between 2.17 and 7.75 grains of water per cubic foot of air will be present at these temperatures and relative humidities.

Other Deterioratives

Fungi and bacteria can be expected in an unprotected silo; the natural environment is favorable to their growth. Silo environment also is favorable to all types of insects and rodents. Certain beetle species are capable of boring through cement; rats and mice can damage or destroy wiring and connectors.

Internal Atmospheres

Equipment within the silo in addition to the missile can provide a source of corrosive atmosphere either through gaseous products or through contact. Fuels emanate vapors, and lubricants deteriorate slowly to produce lighter hydrocarbons as vapors. There may be leakage of hydraulic fluid or liquid propellant drippings that will affect various parts of the missile system.

Fumes may emanate from hydraulic fluids, decomposition of solid fuels or from any hydrocarbon materials used in the missile. Corrosive fumes may be generated by the slow deterioration of rubber compounds or dry film-type lubricants containing molybdenum disulphide.

Corrosion Control Measures

Protective Coatings

Cadmium and zinc platings are mandatory in missiles for sacrificial protective coatings. Conventional zinc chromate primers, the various anodic and chemical conversion films and coatings for the aluminum and magnesium alloys and epoxy resin systems have proven

TABLE 1—Corrosive Agents in Rain Water		
Compound and Source	**Location**	**Concentration mg/l***
Chloride, Cl⁻; major source is sea spray	Over sea or near coastlines 500 miles or more inland	Average 2-20; with extreme winds may increase up to 100 Average 0.1-0.2 but sometimes higher than 1.0
Sulphate, SO₄⁻⁻, major sources in industrial areas	Large cities, industrial areas Other areas	Average 10-50; higher under extreme conditions, i.e., smog 1-5
Nitrate, NO₃⁻	Over land	0.5-5
Hydrogen ions, pH	Over land	Average around 5; near industrial centers it may decrease to 3

* Concentration in rain water in milligrams per liter of some of the most important constituents with respect to corrosion.
Reference: Handbook of Geophysics for Air Force Designers.
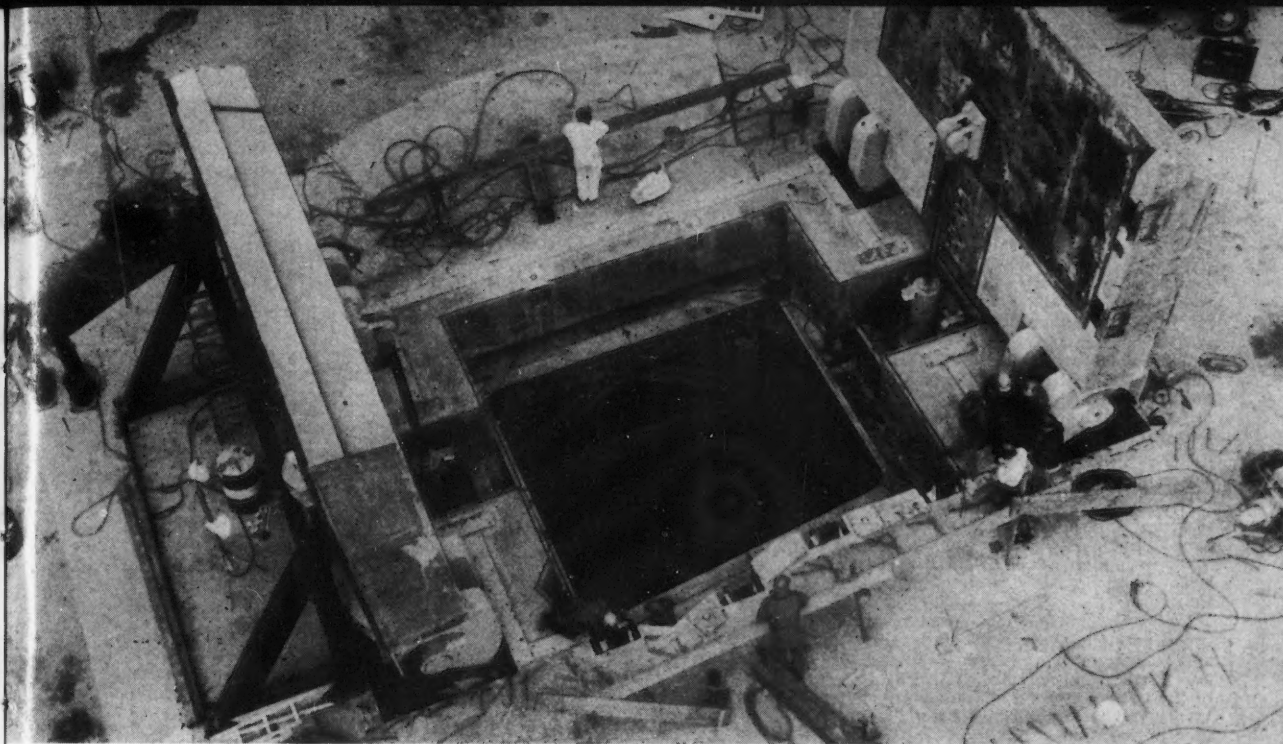
28

resistance to corrosion under various exposure conditions of media, humidity, temperature and time.

Sealing of Silo Walls

Consideration must be given to materials for sealing the walls of a silo. Organic coatings now can be applied in the field in heavier thicknesses with fewer coats than previously possible. Hot spray vinyls, catalyst cured phenolics and epoxies, epoxy modified phenolics and high build alkyd coatings provide satisfactory protection for a wide range of metal, concrete and masonry surfaces. Several coatings afford good resistance to mild acids and alkalies.

Breathing

A method of breathing for the silo cavity must be provided for pressure equalization. Silica gel beds or similar techniques have been perfected for storage tanks and mothballed ships. Such apparatus could be used as an interface device to exclude moisture and still permit breathing. Use of machinery to maintain a dry atmosphere is a better method. Several methods can be used for removal of moisture from air, but conventional refrigerated dehumidification systems are the most suitable because they would be compatible with blower-driven air circulation. Temperature control equipment also would be required to aid the air conditioning system.

Detection Techniques

Because all sources of corrosion cannot be predicted, preventive measures cannot be assumed to be 100 percent efficient. Deterioration presumably commences the moment the missile is stored; detection techniques therefore are necessary to determine the extent of deterioration as it proceeds.

Corrosion detecting and measuring techniques designed to protect missiles in silo storage must meet two essential requirements: (1) Detect corrosion or corrosive conditions before any damage is sustained by the missile, and (2) Accumulate or integrate the total exposure

to corrosive conditions experienced by the missile during the weeks, months or even years it remains in storage.

Visual System

One category of visual inspection for corrosion is the chemical type in which silica gel changes color when the humidity rises above a particular percentage. This does not indicate corrosion, only a humid atmosphere, and indicates only the quality of the atmosphere at the instant of inspection.

A better type of detection is a thin metal film, using a molecularly thin coating of metal on glass or some other substrate. The film corrodes very easily, revealing an integrated history of the corrosive atmospheres. A large number of these inexpensixe thin film indicators can be placed throughout the missile-silo area.

However, the big disadvantage of visual detection is that it cannot be automated and thus recorded at a central point for rapid evaluation.

Electrical Systems

Electrical detection techniques permit continuous readings or recording of humidity or corrosion rate occurring within the silo area.

Progress of corrosion on a metal specimen is determined by measuring the increase in resistance of a thin metal film specimen as the metal is converted from pure metal to oxide.

One significant advantage of electrical detection is that a remote alarm system can be used to indicate corrosive conditions inside the silos.

Measurement of electrical resistance has long been used to determine the extent of corrosion on metal specimens.* Recently work has been done to use electrical resistance measurements to determine corrosion rates in a variety of industrial processes.[1-4] More recently an Air Force program was initiated for development of visual and electrical thin

* See items listed in Bibliography on measuring electrical resistances.

metal film integrating corrosion indicators for storage applications.[5-8]

Readings are made directly on metal specimens without their removal from the corrosive medium. These readings are independent of the temperature and nature of the corrosive medium. This method seems to be the most efficient developed to date.

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FAILURE by corrosion of galvanized domestic hot water storage tanks, a familiar and annoying occurrence to so many householders, is responsible for an economic loss in Canada of several million dollars every year. Because tanks were being replaced in large numbers in post-war housing projects, sometimes within the first year of operation, the Division of Building Research at the request of Central Mortgage and Housing Corporation undertook in 1950 studies of the causes of failure.

The initial investigation involved the detailed physical and metallographic examination of a large number of corroded tanks from a number of localities in Ontario.[1] Subsequently two series of field experiments were planned.

Two Series of Experiments

Series A experiments involved investigation of primary factors of temperature and rate of water consumption with water supplies available at the three localities of Brantford, Peterborough and Belleville.

Series B experiments were planned to investigate the secondary factors of design involving the heater and piping and the resulting conditions of operation of the hot water system as they affected the corrosion of the tanks by the water in Windsor, Ontario.

In Windsor, unusually severe corrosion of galvanized hot water tanks was experienced in two CMHC projects involving 1000 tanks. Half of these were installed in project houses completed in 1948 where the hot water system consisted of No. 30 galvanized tanks, galvanized pipe and 750-w immersion heaters. The remaining half was installed in project houses completed in 1949 where the hot water system consisted of No. 30 galvanized tank, copper piping (including a copper dip tube) and a 750-w immersion heater. After a year there were failures by corrosion of tanks in both projects. Greater frequency of failures in the 1949 project reflected the influence of copper piping. In the 1948 project 65 out of 450 tanks developed leaks in the first year.

Types of Heater Significant

Records of performance of different types of systems in the Windsor area revealed the significant fact that where the tanks were heated by 3 kw side arm heaters equipped with a manual "on" and "off" switch, service life of the tank was much longer than in the cases where the tank was heated by an immersion heater of small capacity.

Series B studies also involved checking effectiveness of corrosion inhibitors such as polyphosphate and silicate in preventing the corrosion of the tanks in this locality.

No attempt was made in either series to observe the corrosion of the piping itself which was copper in some houses and galvanized iron in others.

This article reports results of these two series of field experiments.

Experimental Data

All studies involved complete domestic hot water systems installed in occupied houses in normal use.

Series A

All tanks involved in Series A tests were made to specifications of the

★ Revision of a paper presented under the title "Corrosion of Domestic Hot Water Tanks" at a meeting of Canadian Region Eastern Division, National Association of Corrosion Engineers, Montreal, November 14-15, 1960.
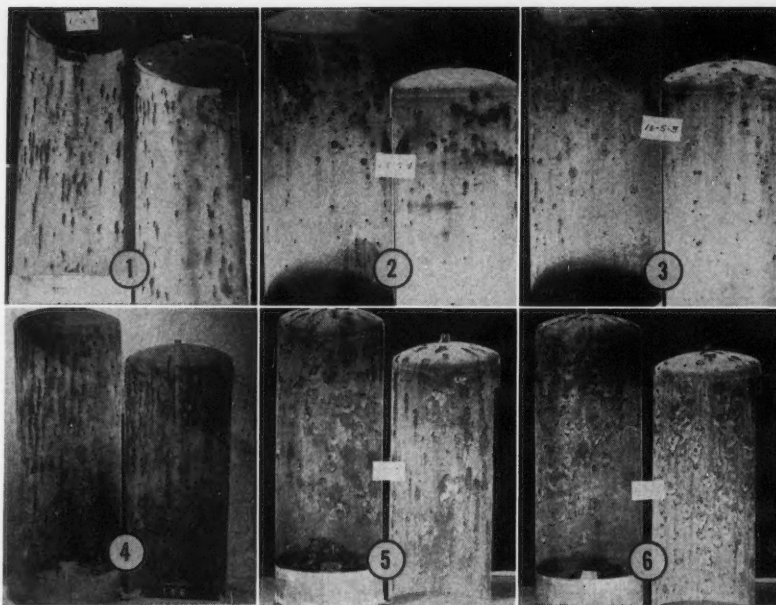
Figure 1—Appearance of tanks after failure at controlled temperatures. Example 1, 23 months at 170 F, Example 2, 17 months at 170 F, Example 3, 20 months at 170 F, Example 4, 80 months at 150 F, Example 5, 66 months at 150 F and Example 6, 60 months at 150 F. Examples 1 and 4 were from the Brantford Project; Examples 2 and 5 from the Belleville Project and Examples 3 and 6 from the Peterborough Project.

Long-Term Tests Show

Design Change Beneficial In Reducing Domestic Hot Water Tank Corrosion★

P. J. Sereda

Division of Building Research
National Research Council
Ottawa, Canada

Hydro-Electric Power Commission of Ontario, designated as 030-1A. They were equipped with two strap-on heaters rated at 800-w each controlled by individual thermostats. Three inches of glass wool insulation was used around the tank. Ten such units were installed in each of the three localities. Half of the units were controlled at 150 F or 160 F and the remaining half at 170 F. Hot water consumption was measured by means of a water meter installed in the cold water supply to the tank.

Copper piping was used in the projects at Belleville and Peterborough; galvanized pipe was used in Brantford. Where copper piping was used, the hot water outlet from the tank was connected with a 6-foot length of ½-inch galvanized iron pipe. The water supply to these units was the regular town supply and analyses given by Leverin[2] give the general type of water involved.

This study was continued for about 6½ years. Many of the tanks had failed earlier. All tanks were removed when they failed or at the end of the 6½-year period and examined physically and

metallographically as described in a previous paper.[1]

Series B

In the two Windsor projects, 50 houses were selected where the hot water systems were altered for the purpose of these experiments. All tanks were replaced with new No. 30 heavy duty galvanized tanks and insulated as before. In a number of these the 750-w immersion heaters were replaced with 3 kw side arm heaters and equipped with an on-off switch operated in the kitchen along with an indicator light which shows when the heater is "on."

Copper piping was replaced with galvanized pipe for a length of about 3 feet from the tank including the dip tube. In a number of these systems a simple dispenser was provided to feed about 10 ppm of either polyphosphate or silicate in Table 1.

After 5 year's service all 50 tanks from the two projects were removed and examined.

Temperature, Copper Pickup and Galvanizing Defects Important

Results and Discussion

Series A

1. There was distinct difference in appearance of the pitting corrosion for each locality as seen in Figure 1.

2. Service life of the tanks varied significantly even when identical installations in one locality were compared.

3. There was an indication that as temperature increased the corrosion rate also increased. This was very definite in the case of tanks from Brantford (Figure 2). Hoxeng and Prutton[3] and Weast[4] came to similar conclusions.

4. Rate of consumption of hot water varied threefold when considering all the units and twofold when considering houses with the same number of occupants. This factor did not seem to influence the corrosion rate. This also was found by Weast.[4] When consumption of hot water from units controlled at 170 F was plotted against the number of occupants in the house (Figure 3), there seemed to be a trend indicating a decrease in the consumption per house as the number of occupants increased. This was a surprising result.

5. Evidence from the metallographic examination was much the same as was obtained in the preliminary work reported.[1] Micrographs from tanks in service in Brantford indicated that there was a reversal of polarity of the steel and zinc. This is in support of the measurements made by Hoxeng and Prutton[3] and Guest.[5] There is also evidence of fissures and separation in the zinc alloy layers. Although the rate of corrosion of the tanks was about twice as rapid at 170 F as at 150 F the micrographs of the tank surfaces at the two temperatures do not reveal differences in the pattern of corrosion (Figure 4).

6. Severe corrosion and early failure was experienced with all tanks operated at the high temperature even though galvanized piping was used in Brantford. This result suggests that copper piping was not the major factor in contributing to the corrosion of these tanks, although it is suspected that the influence of copper piping varies with the type of water used.[6] In Windsor this appeared to be a more important factor just as Newell[7] had found in the case of some New England waters.

7. Thickness of the zinc coating on these tanks varied from 3.5 to 5.5 mils with an average of 4.3 mils. There was no correlation between the zinc thickness and the service life of this group of tanks.

Series B

Results of these tests after 5 years' service can be summarized as follows:

1. Tanks heated by side arm heaters and having galvanized piping showed very little corrosion and appeared in condition to give many more years of service. There was no difference between those inhibited with polyphosphate and those not so protected.

2. Tanks heated by side arm heaters and having copper piping showed more corrosion than those with galvanized piping. Where silicate inhibitor was used there appeared to be less corrosion.

3. Where small immersion heaters were used the corrosion was severe whether copper or galvanized piping was used. Inhibitors in these systems helped reduce corrosion as compared to the identical systems without inhibitor. Although the appearance of pitting corrosion was different with the different inhibitors, it was impossible to determine whether one was more effective than the other in preventing corrosion. It is not certain that the addition of inhibitors was continuous throughout the 5-year period; also, from the work of the American Gas Association,[8] it would seem that the concentrations of inhibitors used were too low for effective protection.

4. Figure 5 shows micrographs of the corroded and uncorroded edges of the sample tanks removed from Windsor. The pattern of the corrosion attack on the zinc, zinc-iron layers and steel interface is the same as that observed previously. The tanks heated by side-arm heaters and having galvanized pipe were corroded least, with an irregular attack on the zinc-rich layer. Tanks heated by side-arm heaters and having copper piping showed increased attack with fissures and pits in the zinc-iron layers and complete lifting of the galvanized layer from the base. Finally, tanks heated by immersion heaters showed very serious disintegration and removal of the zinc-iron layers. Inhibitors had no apparent effect on the pattern of corrosion attack revealed in these micrographs.

General Conclusions

The study at Peterborough, Brantford and Belleville showed that temperature was an important factor in the corrosion of hot water tanks. Reducing the temperature by as little as 10 degrees would certainly add years of service life to the tanks, especially in Brantford.

The study at Windsor showed that design of the hot water system and the resulting manner of operation has great effect upon the extent of tank corrosion. The change from a small capacity immersion heater to a large capacity side arm heater combined with a manual on-off switch was the most effective single factor in decreasing the corrosion of the galvanized tanks in this locality.

Abstract

Corrosion of galvanized tanks was studied in domestic installations in rental housing projects of Central Mortgage and Housing Corporation at Peterborough, Belleville and Brantford, Ontario where sample tanks of the Ontario Hydro-Electric Power Commission were used and at Windsor, Ontario where regular commercial tanks were used. In the first series it was shown that temperature was an important factor affecting the corrosion. In the series conducted at Windsor it was shown that when 3-kw side-arm heaters were used instead of small immersion heaters the design change was the greatest single factor in reducing corrosion.

Copper piping was shown to have an influence upon the corrosion, especially if a copper dip tube was used inside the tank. Results from tests involving corrosion inhibitors were inconclusive, perhaps because the concentration of about 10 ppm was too low.

Micrographs of the galvanized coatings show that the corrosion attack was very irregular, starting with fissures and separating the zinc-iron layers from the base. These fissures appear even in the uncorroded edges indicating they are produced in the galvanizing process and that changes in this process may improve the corrosion resistance. Reversal of potential between the steel and the zinc also is apparent in some micrographs.   7.5.5

Figure 2—Service life of tanks controlled at different temperatures.
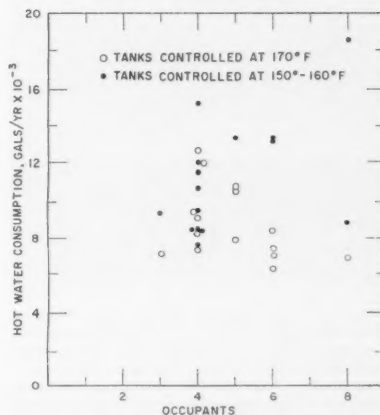
Figure 3—Rate of hot water consumption as related to number of occupants in the household. (Taken from Brantford, Belleville and Peterborough Projects)

TABLE 1—Details of Experimental Hot Water Systems in Windsor

Project Year	No. of Systems	Piping	Heater	Inhibitor
1948	5	galv.	3 kw side arm	none
1948	10	galv.	3 kw side arm	polyphosphate
1948	10	galv.	750 watt Immersion	polyphosphate
1949	5	copper	3 kw side arm	none
1949	10	copper	3 kw side arm	silicate
1949	10	copper	750 watt Immersion	silicate

Hot Water Tank—

(Continued From Page 31)

There is some evidence that copper piping, even when stopped three feet from inlets and outlets of tanks, has some effect upon their corrosion in the Windsor area.

Although inhibitors were effective in prolonging life of galvanized tanks in Windsor heated by small immersion heaters, they were not nearly as effective in preventing corrosion as was the design change and the related change in service conditions. Thus, it is believed that much can be done to reduce corrosion of galvanized tanks by changing the system design and operating at the lowest temperature possible.

Metallographic examination of the corroded galvanized coating shows it is attacked irregularly as evidenced by horizontal and vertical cracks and fissures which often cause separation of zinc layers from the base, thus affording no protection at a time when much of its original volume remains. Because these fissures appear even in the uncorroded side of the tank they must be the result of faults produced during application of the galvanized coating.

It may be that corrosion begins at these faults. In any case it is evident that the protection this galvanizing layer offers to the steel is not what would be expected. These observations, therefore, indicate an area of fruitful future research.
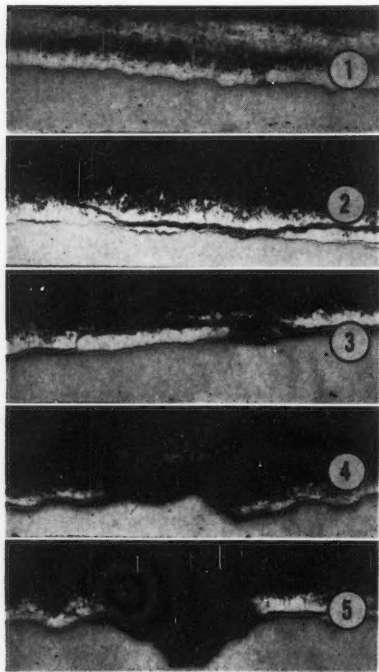
Figure 4—Micrographs from tanks removed from Brantford showing the characteristic corrosion attack on the galvanized coating. Magnification 96X. Number One shows an uncorroded edge. Numbers Two and Four are examples of a corroded edge from tanks operated at 170 F with failure after 3 years' service. Numbers Three and Four are of corroded edges from tanks operated at 150 F with failure after 6½ years' service. Number Five indicates a reversal of polarity.

Acknowledgment

(EDITOR'S NOTE: An interesting discussion of glass-lined water heater corrosion will be found beginning on Page 9, September, 1960 issue of CORROSION.)

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About $300 million worth of high fidelity sound equipment was sold in the United States during 1959.

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Farmers in the United States produced 1.4 billion bushels of wheat and 3.8 billion bushels of corn in 1958.

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Technical Topics
on
Chemical Industry
Scheduled for Publication

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Figure 5—Micrographs of galvanized tanks removed from Windsor, Ontario. Number One is an uncorroded edge (96X). Number Two is a side arm heater with galvanized piping (161X). Numbers Three and Four are side arm heaters with copper piping, silicate inhibitor (161X). Numbers Five and Six are immersion heaters with copper piping, silicate inhibitor (96X and 161X respectively). Numbers Seven and Eight are immersion heaters with galvanized piping, phosphate inhibitor (161X).

Houston Field Office Offers OTS Reports Related to Corrosion

Several reports of probable interest to corrosion engineers, including translations of foreign technical literature, are available from the U. S. Department of Commerce's Houston Field Office, 610 Scanlan Bldg., 405 Main St., Houston 2, Texas. These reports published by the Office of Technical Services are listed below with publication number and prices:

Soviet Non-Ferrous Metallurgy: Selected Translations No. 10 (60-11878) $1.50.

Rare Elements as Alloying Additives to Heat-Resistant Steel (60-31226) 50 cents.

Selected References on Brittle Fracture (PB 161205) 50 cents.

Fatigue Data on Precipitation-Hardenable Stainless Steels (PB 161196) 50 cents.

Thin Metal Films as Corrosion Indicators (May, 1959) Tests of more than 1100 thin metal films to determine their value as corrosion indicators for packaged material are evaluated in this report and the following one also (PB 151974) $1.50.

Thin Metal Films as Corrosion Indicators (March 1960) (PB 161757) $2.

Metallurgical and Mechanical Characteristics of High-Purity Titanium-Base Alloys (PB 161817) $3.

Phase Relationships in Selecting Binary and Ternary Vanadium-Base Alloys systems (PB 161816) $2.

Copies of the following lists of translations of foreign technical literature are available free on request:

Chemical engineering physical, analytical and organic chemistry, bio-chemistry and fuels (OTS 60-354)

Metals (OTS 60-357)

Continuous Production Is Developed for Sheet Metals

A new process for continuous production of commercial sheet metals and alloys is being developed at Stevens Institute of Technology, Powder Metallurgy Laboratory, Hoboken, N.J. The process is expected to save time, reduce costs and increase plant efficiency.

Metal and alloy sheets now are produced commercially in several separate operations which require multiple heating and compressing of large metal billets or ingots. In the new process, metals or alloys in the form of fine powders are suspended in a liquid. The resulting suspension known as a "slip" or "slurry" resembles the pulp suspension used in the paper manufacturing. The "sheets" so produced are passed continuously through controlled atmospheric furnaces where the sheets are brought to temperatures just below their melting point. Called sintering this heating consolidates the sheets which are then passed through mechanical rollers. Subsequent heating brings the sheets to required density.

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The 11th National Chemical Exposition, sponsored by the Chicago Section of the American Chemical Society, will be held September 5-8 at the International Amphitheatre in Chicago.

THICK COATINGS can be sprayed on floors at a rate five times that of the usual trowel method as shown above. Catalyzed coatings mixed with fillers such as silica and aluminum oxide are sprayed by the new gun as thin as 1/16-inch to any desired thickness, according to the developer, Carboline Company.

Thick Catalyzed Floor Coatings Applied With New Spray Gun

A new spray gun has been developed for applying thick floor coatings of catalyzed materials mixed with fillers such as silica and aluminum oxide.

The gun is said to apply floor coatings five times faster than the conventional trowel method. Coatings can be sprayed at thicknesses from 1/16-inch to any desired thickness in one coat and to 3/32-inch on vertical surfaces, according to the developer, Carboline Company, 32 Hanley Industrial Court, St. Louis 17, Mo.

In addition to cutting plant shutdown time for floor coating operations, the gun also reduces application costs. The average application cost of trowelling is about 20 cents per square foot; spray application cost is about 5 cents per square foot, according to Carboline.

The accompanying photograph shows a comparison of the areas that can be coated with the gun and with a trowel at the same time.

The floor spray gun has a 10-gallon tank. The mixed coating material is forced by air pressure through a 2-inch flexible hose to a spray nozzle that is designed to give a round spray pattern.

American Ceramic Society Enamel Division to Meet

High temperature protective ceramic coatings and ceramic coatings as adhesives will be among the subjects for the September 20-23, 1961, meeting of the Enamel Division of the American Ceramic Society to be held at the French Lick-Sheraton Hotel, French Lick, Ind. Other subjects will include ceramic-metal composites, flame-sprayed ceramic and cermet coatings for metals and ceramic coatings on dielectrics.

Additional information can be obtained from the American Ceramic Society, 4055 North High St., Columbus 14, Ohio.

Stainless Headers Give 15-Year Sulfur Service

To test their theory that cast stainless steel sections of sulfur dioxide headers would give long service life and to avoid making a major, expensive revision in construction, engineers at the Weyerhaeuser Company's sulfite plant at Everett, Wash., replaced a 90-degree flanged elbow in the header system made of high chromium cast iron with a Type HH cast stainless alloy.

The cast stainless elbow, installed over 15 years ago, is still in operation. Because of this favorable service life, iron headers are being replaced, section by section, with Type HH Alloy castings.

The headers carry hot, corrosive sulfur dioxide gas from a sulfur burner to the cooling pond—a step in the manufacture of cooking acid used in the sulfite puiping process. Under these corrosive conditions, the original headers made of chromium cast iron had to be replaced every 2 to 2½ years.

BOOK NEWS

Atmospheric Emissions from Petroleum Refineries. 56 pages, 5¾ x 9¼ inches. paper. 1960. Pub. Health Pub. No. 763. Superintendent of Documents, U.S. Govt. Printing Office, Washington 25, D.C. Per copy, 30¢.

A publication of the Division of Air Pollution, Public Health Service, U.S. Dept. of Health, Education and Welfare. A guide for the measurement and control of emissions from refineries. The book is based principally on the findings of a "joint project" for the study of atmospheric pollutants produced by oil refineries in the Los Angeles area.

The book deals with petroleum refining, including distillation, conversion, treating and blending; atmospheric emissions, involving sources, such as those from storage tanks, catalyst regeneration units, compressor engines, boilers and process heaters, air blowing, acid treating; control of emissions, involving process changes, economics, estimates of emissions.

Eleven references are given. Appendices give methods for calculating hydrocarbon vapor losses, control methods and a glossary. There are 13 tables and 13 illustrations.

Ultrasonics and Its Industrial Applications. By O. I. Babikov, 224 pages, 6 x 9 inches. Translated from the Russian. 1960. Consultant's Bureau, Enterprises, Inc., 227 West 17th St., New York 11, N.Y. Per copy, $9.75.

A translation of the original Russian text published by the State Press for Physicomathematical Literature in Moscow in 1958. Included are propagation and absorption of ultrasound, including concept of oscillations, velocity of sound, reflection, cavitation and visual observation;

Generation considerations include mechanical, magnetostriction and piezoelectric effects; pulse methods for ultrasonic flaw detection consider circuits, parameters, determining sizes of defects, quality control, examples of application;

Ultrasonic flaw detection with undampened oscillations covers the shadow method, examples of shadow method applications; resonance method with examples;

Investigations of microstructure are covered in one chapter and another chapter is devoted to ultrasonic pulse methods of physical chemical analysis, including influence of slow-moving liquids, and impurities. Other chapters are headed machining of hard and brittle materials, aluminum soldering and plating, ultrasonic cleaning and metallurgical effects of ultrasonic processing.

There is a bibliography of 202 references and 149 figures.

1956 Bibliographic Survey of Corrosion. NACE Publication No. 60-12. 248 pages, 8½ x 11 inches, plastic binding for flat opening. Compiled by Nicole Treves Atlas. 1960. Published by National Association of Corrosion Engineers, 1061 M & M Bldg., Houston 2, Texas. Per copy: non-members NACE, $27.50; members $22.50.

A collection of 2136 abstracts of technical literature published during 1956 in numerous periodicals over the world related to articles, books and pamphlets on corrosion and corrosion control. Also included are a small number of abstracts

of material published in earlier years not previously included in bibliographies. Abstracts used were selected from those prepared by 31 agencies which have authorized the National Association of Corrosion Engineers to use their abstracts.

Abstracts are arranged in the book according to their principal content as classified under the NACE Abstract Filing Index. In this index the literature is classified under eight main headings: General, testing, characteristic corrosion phenomena, corrosive environments, preventive measures, materials of construction, equipment and industries. Each of these groups is further subdivided.

Each of the subject categories into which the abstracts are grouped is cross-indexed. An extensive subject index is largely supplementary to the cross-indexing, providing access to the data through many metals and alloys by trade names, specific properties and behavior in specific media.

The author index lists 2859 names.

Referencing is to page and abstract on the page by number.

An appendix gives information to assist users in obtaining copies of articles in which they are interested.

This is the seventh in a series of NACE bibliographies on corrosion control literature covering the period 1945-56. A total of 22,181 abstracts is included in all volumes.

Nondestructive Testing in the Missile Industry. 71 pages, 6 x 9 inches, hard covers. Sept. 1960. Special Tech. Pub. No. 278. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. Per copy $2.

Seven of the eight papers presented at the Symposium on Nondestructive Testing in the Missile Industry, sponsored by ASTM Committee E-7 on Nondestructive Testing, Monday, October 12, 1959. Three of the papers deal with radiographic methods applied to large solid propellant rocket motors, high energy radiography and of weldments in motion. One paper deals with field testing of missiles and aircraft and two concern ultrasonic methods to determine flaws and defects. One paper concerns, among other things, ultrasonic testing of fluids to detect foreign particles.

Saline Water Conversion. 246 pages, 6 x 9¼ inches, paper. 1960. No. 27, Advances in Chemistry Series. Special Issues Sales, American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C. Per copy, $5.85.

Twenty-two papers comprising the Symposium on Saline Water Conversion before Div. of Water and Waste Chemistry, 137th National Meeting, American Chemical Society, Cleveland, April 1960. Papers cover theoretical and large scale tests of various sea water conversion schemes, including economics. Of interest to corrosion workers is the paper "Corrosion of Metals in Sea Water," by F. W. Fink, Battelle Memorial Inst., Columbus, Ohio. The paper discusses generally theories of corrosion by sea water with respect to macro-organisms, concentration cells, velocity, cavitation. Metals considered include ferrous-base, aluminum and its alloys, stainless steels, non-ferrous alloys, titanium. Protective coatings and cathodic protection are mentioned briefly. Design considerations of heat exchangers, pumps, erosion-corrosion are mentioned.

PLASTIC COATED steel pipe was used to resist the corrosive coal field soil and swampland in Kentucky, where this natural gas line is being installed. Republic Steel Corporation's high density polyethylene coating called X-Tru-Coat was extruded over the steel pipe at the mill.

Plastic Coated Pipe Installed to Resist Coal Field Soils

More than 22 miles of plastic coated steel pipe have been installed through highly corrosive coal field soil and swampland in Kentucky. The line will carry natural gas to the towns of Corbin and London.

The most corrosive agent along the line is the acid formed by rain and other moisture draining through piles of coal slag. The plastic coating, a mill applied, high density polyethylene called X-Tru-Coat, extruded over the steel pipe by Republic Steel Corporation, 1441 Republic Bldg., Cleveland 1, Ohio, is designed to protect the pipe permanently, thus reducing the cost and need for pipe replacement and maintenance.

During installation, where rocky soil was encountered, the coating withstood the scrapes and abrasions from handling, according to the installation contractor, Cumberland Contracting Company of Monticello, Ky.

The pipe was shipped from the steel mill with the coating cut back sufficiently on each length to allow for welding. A pressure sensitive plastic tape was wrapped on the job to protect the exposed areas of the welded joints. A holiday detector was passed along the pipeline to find coating breaks.

The pipe is 65⁄8-inches in diameter and will operate at 350 pounds per square inch.
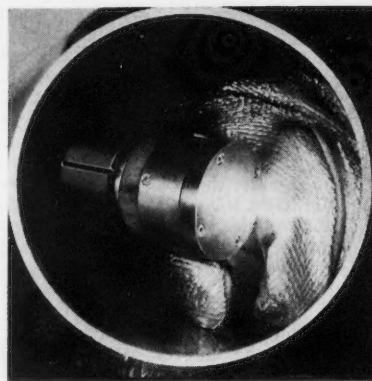
COMPACT ARC-PLASMA spray gun has been designed for depositing refractory coatings on internal surfaces of small diameter cylinders and tubing. Only 2 inches long and 1½ inches in diameter, weighing less than one pound, the small gun has been used to spray corrosion resistant and high temperature coatings on interior walls of small rocket nozzles, cylinders and chambers. The gun was developed by Plasmadyne Corp., 3839 S. Main St., Santa Ana, Cal.

Industrial Engineers Set May 11-13 Detroit Meeting

The Detroit Chapter of the American Institute of Industrial Engineers will be host for the institute's 12th Annual National Conference and Convention to be held May 11-13 at the Sheraton Cadillac Hotel. Additional information can be obtained from James E. McCartney, Room 29, 4181 Oakman Blvd., Detroit 4, Mich.

Tin Plated Steel Used Instead of Lead To Protect Cables

The same tin-plated steel used in tin cans for foods and beverages is being used as a moisture barrier to protect telephone cables. These cables running from central exchange offices to customers' telephones may have 2000 pairs of wires, each insulated with paper. Whether hung from poles or buried in the ground, these wires must be protected from moisture.

A continuous jacket of tin-plated steel, soldered tight, is being used for this moisture protection at a lower cost than the conventional lead-sheathed cable, according to Jones & Laughlin Steel Corporation, 3 Gateway Center, Pittsburgh 30, Pa., manufacturer of the tin sheath.

The paper covered pairs of fine copper wires in the cable are bound together with strong paper tape. A thin sheet of corrugated aluminum around the core serves as an electrical shield and lightning protector. A ribbon of tin plate is then corrugated and longitudinally wrapped around the cable on high speed machines that automatically solder the tin plate into a moisture resistant sheath at a rate of about 100 feet per minute, as shown in the accompanying photograph.

After a coating with an asphalt-rubber compound and polyethylene, the completed cable is ready for use.

This type cable sheath was developed by engineers at Western Electric Company, Kearny, N.J., manufacturing unit of the Bell Telephone System.

TIN PLATE jacket and inner layer of corrugated aluminum emerge from automatic telephone cable sheathing machine. The two materials are formed around the paper wrapped cable core. The tin plate is soldered to form a moisture resistant sheath. An asphalt-rubber compound and polyethylene outer coating is used for additional protection.

Belgian University Offers Course on Corrosion

A course on corrosion is being offered at the University Libre de Bruxelles, Belgium. It began in November and will run for several months. The course totals 20 lectures. Lectures will be followed by laboratory work and seminars, which will deal primarily with questions asked during the course.

BETTER COATINGS THROUGH RESEARCH

RESEARCH EFFORT: *To continue improving Plasticap coatings and application methods.*

RESULTS: *A series of successfully completed research projects and an expanded research program. Here are some of these results:*

● Additional new research facilities and personnel have been added recently to augment the continuous research program conducted for years by Plastic Applicators and independent research organizations under contract to Plastic Applicators. Man hours and dollars devoted to research have been constantly increased.

● New coatings developed through this research program have been introduced regularly. Most recent new coating released from the laboratories is Plasticap HTP, which was developed to provide lasting resistance to acids and caustics, even at temperatures above 350°F.

● Air dehydrators have been installed at all Plastic Applicators plants because research has shown that removing all water, oil, and other impurities from air used in the application of Plasticap coatings improves adhesion and resistance qualities of the coatings.

PROTECT YOURSELF AND YOUR PIPE. SPECIFY PLASTICAP. MORE TUBULAR GOODS ARE PROTECTED WITH PLASTICAP THAN ANY OTHER COATING.

Plasticap

PLASTIC APPLICATORS, INC.

REGD. T.M.
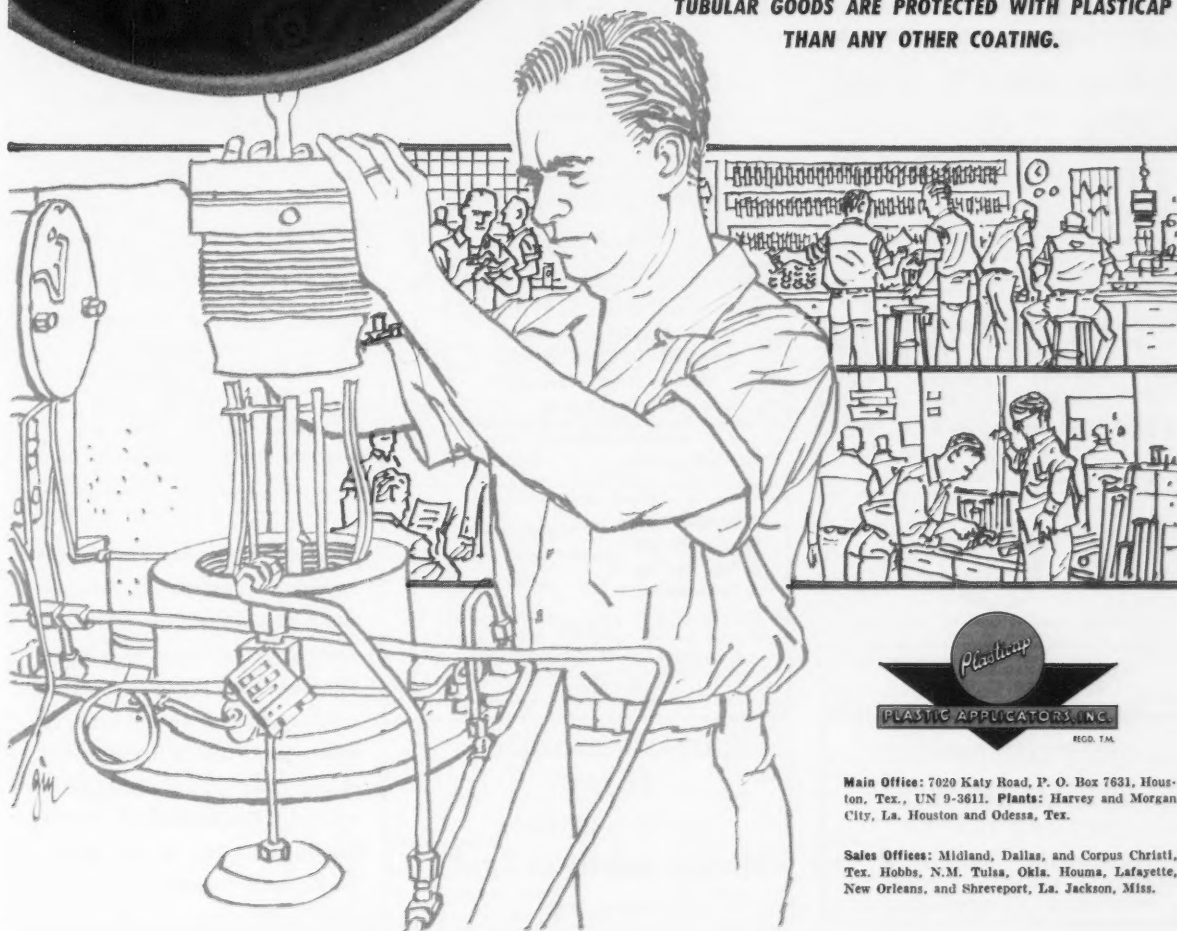
Main Office: 7020 Katy Road, P. O. Box 7631, Houston, Tex., UN 9-3611. **Plants:** Harvey and Morgan City, La. Houston and Odessa, Tex.

Sales Offices: Midland, Dallas, and Corpus Christi, Tex. Hobbs, N.M. Tulsa, Okla. Houma, Lafayette, New Orleans, and Shreveport, La. Jackson, Miss.

High Production Techniques Used to Cast Aluminum Fan

An industrial fan in sizes from 54 to 120 inches in diameter is being cast by a high production technique rather than the sand cast method. The one-piece, heat-treated blades are made of aluminum alloy for lightness and resistance to fatigue and corrosion. A separate ductile cast iron hub can be installed by itself and the blades bolted into position later to save installation and maintenance time

The blades, containing 7 percent silicon and 0.3 percent magnesium have an endurance limit of 13,000 psi as compared with 8500 psi for sand cast blades, according to the designer, Metal Products Division of Koppers Company, Inc., 200 Scott St., Baltimore, Md.

The fan will have probable use on high performance radiator-type cooling equipment, air conditioning and refrigeration units and diesel locomotives.

PERIODICALS

Dissertation Abstracts. Vol. XX, No. 11. Monthly Periodical. 8¾ x 10⅞ inches Published by University Microfilms, Inc., 313 N. First St., Ann Arbor, Mich. Vol. XX, $20, in U.S.; $22, Foreign.

A periodical containing abstracts of doctoral dissertations from graduate schools cooperating with the publishers. The abstracts are classified under a number of headings, ranging from Agriculture, Anatomy, through Zoology. Each abstract includes a notation of the cost of obtaining from University Microfilms either microfilm or Xerox copies of the entire dissertation.

The 13th International Chemical Engineering Exposition and Congress, ACHEMA 1961, will be held June 9-17 in Frankfurt am Main, Germany.

February ASHRAE Meeting

Corrosion of air conditioner components will be the topic for one of informal discussions forums at the February 13-16 semi-annual meeting of the American Society of Heating, Refrigerating and Air-Conditioning Engineers to be held at the Conrad Hilton Hotel in Chicago, Ill.

Hawaiian Corrosion Firm

Plastics Engineering of Hawaii, 1529 Kalakaua Ave., Honolulu, began operation of its new plant last month. Headed by NACE member R. D. Jackson, the company is a contractor for plastic coatings and linings for corrosion prevention.

The week of February 19-25 has been designated as Engineers' Week by the National Society of Professional Engineers.

NEW PRODUCTS

Ceramics

Precision ceramic casting of large metallic products with high strength and close dimensional tolerances is described in a brochure available from Shaw Process Development Corp., 82 Shore Rd., Port Washington, N. Y. Porosity, cracks, surface inclusions and other conventional foundry problems are said to be eliminated by use of a ceramic mold with a microscopic network of cracks which accommodates expansion of the ceramic particles and allows gases to escape.

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Corrosion resistance of commercial glasses is discussed in a booklet titled "Properties of Selected Commercial Glasses," available from Corning Glass Works, Corning, N.Y. Information on several new glasses also includes thermal expansion, optical properties, thermal stress, heat transmission, electrical properties and viscosity data.

Cleaners

Removal of paint from galvanized steel without attacking the zinc is claimed for Chemclean No. 441B, a mixture of strongly alkaline salts used at 8 to 16 ounces per gallon of water at 180 to 200 F in a mild steel tank. This cleaning solution strips the paint film from metal and leaves a surface that can be re-painted without further treatment, according to the developer, Chemclean Products Corp., 15-08 121 St., College Point 56, N.Y. It will remove alkyds, malamines, phenolics, urea, urea formaldehyde resins and other synthetic paints, according to Chemclean.

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Console type ultrasonic cleaners with stainless steel tops have been designed for use in laboratories and hospitals. Available with one, two and three chambers, the cabinets are mild steel with tops and tanks of Type 304 stainless steel. The cleaners are produced by National Ultrasonic Corp., 111 Montgomery Ave., Irvington 11, N.J.

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Two new dry-type chemical treatments for boiler and process system cleaning operations are based on sulfamic acid. They are an alkalinity-pH depressant and an acid cleaner recommended for cleaning boilers, heat exchanger, condensers, evaporators, cooling jackets, process vessels and piping, according to the manufacturer, Ionac Chemical Co., Birmingham, N.J.

Coatings, Metallic

Selective plating process that permits deposit of many metals and alloys on most any conductive basis material is being marketed by Selectrons, Ltd,. 520 Fifth Ave., New York 36, N.Y. Thicknesses can be controlled with precision and can be limited to areas where the plate metal is needed, according to Selectron. Equipment used includes a special power pack, plating styluses and non-toxic, basic electrolytes.

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Chemical deposition of protective tin coatings on metal surfaces at temperatures lower than hot dip process and without the use of electricity is claimed for a new process developed by Shipley Company, Inc., Walnut St., Wellesly 81, Mass. A chemical called Cuposit LT-26 produces a stable solution to permit quick dipping, according to the manufacturer. Tests have shown that this chemical can be used to eliminate most soldering problems on printed circuits, eyelets, connectors, plugs and other electronic hardware. Other applications are under development.

Coatings, Organic

A single-package epoxy enamel for maintenance coating on surfaces and equipment exposed to alkali and acid fumes has been developed by E. I. du Pont de Nemours & Company, Wilmington, Del., under the trademark Corlar. This new epoxy is designed to eliminate mixing in the field and the problem of limited pot life of catalyzed epoxy formulations. Available in white and nine colors, Corlar can be applied by brush, roller or spray, dries tack-free in six hours and is recommended for wood, masonry and metal.

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A high-build vinyl coating for application with conventional or airless spray equipment has been developed by Amercoat Corporation, 4809 Firestone Blvd., South Gate, Cal. When applied with airless spray equipment, only one cross sprayed coat of this new material called Amercoat No. 99 is required to obtain a dry film thickness of about 5 mils. Two coats are required to give a dry film thickness of 5 mils with conventional spray equipment, according to Amercoat. It is recommended for use on tank exteriors, ship hulls and all types of structural steel and can be applied over organic primers.

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Epothane base coating systems designed to give durable tile-like finishes on glass, metal, concrete, composition or wood surfaces is being manufactured by Forboil Company, 801 Key Highway, Baltimore 30, Md. The coating can be applied by brush, roller or spray.

Metals, Ferrous

Birdsboro Corp., Birdsboro, Pa., has converted its steel foundry production from acid open hearth furnaces to basic electric melting process. Formerly limited to carbon and low alloy steels, the company now can make foundry type stainless and high alloy steels for high temperature, high pressure and corrosion resistant applications.

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Mechanical properties and corrosion resistance of Pitt-Ten, a new light weight, high strength structural steel are described in a brochure offered by Pittsburgh Steel Co., Box 118, Pittsburgh 30, Pa. Also included are chemical properties and engineering data.

Non-Metallics

Expected uses of a new high temperature, flexible felt material made of plain and reinforced graphite and carbon include insulation, gas filtration and gasketing, according to an information bulletin

NEW PRODUCTS

letin available from National Carbon Company, 270 Park Ave., New York 17, N.Y. These new non-woven forms of flexible graphite and carbon are produced by processes similar to those used in the manufacture of graphite cloth. The bulletin includes data on permeability, resistance, density, strength, gage and weight for four grades each of graphite and carbon felt now available.

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A new grade of carbon-graphite with greater resistance to oxidation and high temperature for use as parts that must operate in oxidizing atmospheres at temperatures to 1200 F has been developed by United States Graphite Company, Saginaw, Mich. Called Graphitar, the new grade has a lower coefficient of friction, improved wear resistance and greater stability over previous grades, according to the company.

Pipe

Wider range of sizes and types of SoundZorber rubber pipe are being manufactured by General Rubber Corporation, 64 Summit St., Tenafly, N.J. This flexible pipe is designed to control noise and vibration on pressure and vacuum pipe lines. Pipe walls are wire-reinforced and made from multiple plies of rubber-impregnated fabric embedded in rubber. Inner lining is of high tensile, abrasion resistant rubber.

Seamless, small diameter tubing made from Ni-O-Nel, an International Nickel Company alloy containing 42 percent nickel, 21 percent chromium and small amounts of molybdenum and copper, is being fabricated by Superior Tube Company, 1717 Germantown Ave., Norristown, Pa. This tubing is designed for metal-arc, inert gas or resistance welding and can be machined in the annealed condition. It has good resistance to corrosion by hot sulfuric, sulfurous and phosphoric acid solutions and also resists nitric acid solutions, nitrates and the cupric, ferric and mercuric salts except chlorides, according to Superior Tube.

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Hill Hubbell Company, 3091 Mayfield Rd., Cleveland 18, Ohio, pipe coating and wrapping contractors, has been licensed to apply Republic Steel Corporation's X-Tru-Coat, a continuous polyethylene plastic jacket extruded over an adhesive that bonds to the steel pipe. Hill Hubbell will expand its three plants in Youngstown and Lorain, Ohio, and Hammond, Ind., to handle the new process.

Plastics

A polyester packaging material that is heat sealable and treated with a volatile corrosion inhibitor is being produced by Daubert Chemical Company, 4700 South Central Ave., Chicago, Ill. Called Nox-Rust Clear-Pak, the treated plastic protects packaged ferrous metal parts from rust and corrosion by releasing an inhibitor vapor into the package, according to the Daubert Company. The transparent plastic used is Mylar, produced by du Pont.

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A new vinylidene fluoride resin called Kynar is being marketed by Pennsalt Chemicals Corporation, 3 Penn Center, Philadelphia 2, Pa. This fluorine-containing thermoplastic resin is designed for long life and high performance in environments which degrade less stable materials. Chemically, Kynar is a crystalline, high molecular weight polymer of vinylidene fluoride containing over 59 percent fluorine by weight. Data from standard laboratory tests and functional evaluations of fabricated parts indicate Kynar to be mechanically strong, resistant to distortion and creep at low and high temperatures, resistant to corrosive chemical attack, flame resistant and stable under extreme conditions of weather and ultraviolet radiation, according to Pennsalt.

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A 22-page "Guide to Man-Made Fibers" is included in the 1961 edition of "Fiber Facts," a small pocket-sized digest available from American Viscose Corporation, 1617 Pennsylvania Blvd., Philadelphia 3, Pa. The guide includes definitions, physical properties and a summary of characteristics and applications.

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Rectangular vinyl caps have been designed to keep out moisture, dust and contaminants in miniature electronic connectors during manufacture, shipment, storage and service. The caps are manufactured by S. S. White Industrial Division, 10 East 40th St., New York 16, N.Y.

About 72 brands of cleaning products for use in the home were on sale at USA supermarkets in 1959.

Kennametal, Incorporated, Latrobe, Pa.

SARAN LINED PIPE—no failure in nine years
carrying 15,000,000 gallons of hot acid!

When a process uses hundreds of gallons a minute of hot corrosive acids . . . including concentrated hydrofluoric . . . trouble-free production depends on the corrosion resistance of piping. The Saran Lined Pipe shown above keeps its hot acid cargo flowing, year-in, year-out, without failure.

At the Latrobe, Pa., plant of Kennametal, Inc., hundreds of feet of Saran Lined Pipe and valves carry concentrated hydrochloric (20° Baumé) and hydrofluoric (70%) acids, as well as acidic metallic salts, between processing stations. Solution temperatures reach as high as 150° F., with some sections of the pipeline exposed to outdoor temperatures. Says Robert R. Nagel, Manager of Metallurgical Operations, "Saran Lined Pipe gives a permanent installation, with less maintenance than any other pipe we've tested. For the past nine years, we've had no failures at all, even where there's vibration from pumps in the line.

"Saran Lined Pipe has a strong steel casing that supports itself. It won't crack from accidental blows, an important safety factor for our operating personnel, considering the corrosive materials we handle. We even use Saran Lined valves with other pipe systems because we consider them leak-proof."

For dependable piping systems that will stand up under even the most corrosive of chemicals, consider Saran Lined Pipe. Saran Lined Pipe, fittings, valves and pumps are available for systems operating from vacuum to 300 psi, from below zero to 200° F. They can be cut, fitted and modified easily in the field without special equipment. For more information, write Saran Lined Pipe Company, 2415 Burdette Avenue, Ferndale, Michigan, Dept. 1565AU2.

THE DOW CHEMICAL COMPANY ◆ DOW ◆ Midland, Michigan

MEN in the NEWS

Robert M. Lewis, David L. Leonard and **Thomas F. Regan** have been named as technical representatives in the Metropolitan New York area for Union Carbide Plastics Company, Division of Union Carbide Corporation. They will have headquarters at the company's office, 1051 Bloomfield Ave., Clifton, N. J.

Three appointments have been made in the Department of Metallurgy at Pennsylvania State University. **Robert W. Lindsay** has been promoted to head of the department. **Earle R. Ryba** and **John H. Hoke** have been appointed assistant professors.

Two industrial regional managers have been named for Permatex Company, Inc., 300 Broadway, Huntington Station, N. Y. **John J. McGroarty**, 8702 Oasis Ave., Westminster, Cal., is manager of the western region; **Michael L. Sullivan**, 9520 Thanksgiving Dr., Miami, Fla., is manager of the newly created southeastern region.

William A. Mudge, formerly with International Nickel Co., Inc., has become a lecturer in metallurgical engineering at New York University's College of Engineering, Washington Square Center, New York 3, N. Y.

Eugene H. Ott, director of resin research and production for the Ferbert Schorndorfer Division of the American Marietta Co., Cleveland, Ohio, has been elected president of the Federation of Societies for Paint Technology.

Austin J. Paddock has been appointed administrative vice president of fabrication and manufacture for United States Steel Corp., Pittsburgh, Pa. He will be in charge of the American Bridge, Consolidated Western Steel, Universal Atlas Cement and U. S. Steel Homes Divisions. **J. Donald Rollins** has been appointed president of the American Bridge Division.

Robert C. Reese has been appointed supervisor of product engineering for plant equipment products at Corning Glass Works, Corning, N. Y.

William H. Schneider, Jr., has been appointed district manager of Pittsburgh Corning Corporation's Chicago office, 205 West Wacker Dr., Engineering Bldg., Chicago, Ill.

Frank W. Silva has been named manager of construction for B. F. Goodrich Chemical Co., 3135 Euclid Ave., Cleveland 15, Ohio.

Willis F. Thompson, executive vice president of Westcott and Mapes, Inc., New Haven, Conn., has been elected president of United Engineering Trustees, Inc., 29 West 39th St., New York 18, N. Y.

C. V. Sternling of Shell Development Co., Emeryville, Cal., has been awarded the AIChE Allan P. Colburn Award for basic research in the petroleum industry.

Pierce Hollingsworth has been appointed manager of the Industrial Gas Cleaning Department, Metal Products Division, Koppers Company, Inc., 200 Scott St., Baltimore 3, Md.

William Winfield Walton has been appointed chief of the Organic Building Materials Section of the Building Research Division of the National Bureau of Standards, Washington 25, D. C.

O. C. Mudd, formerly chief corrosion engineer for Shell Pipe Line Corp., now is associated with Pipeline Technologists, Inc., 3431 West Alabama, Houston, Texas. Recently he went to Sydney, Australia, on a 2-year project assignment.

Howard E. Abrams has been appointed manager of the laboratory for Pall Corporation, 30 Sea Cliff Ave., Glen Cove, N.Y.

Alan Law has been appointed chief industrial engineer and head of the newly created Industrial Engineering Department of the Graver Tank & Mfg. Co., division of Union Tank Car Company, 4809 Tod Ave., East Chicago, Ind. **R. W. Briska** has been appointed plant engineer under Mr. Law. **E. G. Vail** has been promoted to manager of the company's plant in Houston, Texas.

NACE Member **Jack A. Harrison** has been promoted to general sales manager for Hill Hubbell Co., 3091 Mayfield Rd., Cleveland 18, Ohio. **Howard Trusler** has joined the company as district sales manager, covering Ohio, West Virginia, Kentucky and parts of Pennsylvania. **M. M. Bowen, Jr.**, has been appointed district sales manager for North and South Dakota, Nebraska, Kansas, Iowa, Missouri and Minnesota. He will be based at Omaha, Neb.

David M. Jacks and **Thomas G. Cocks** have been named vice presidents of Nalco Chemical Co., 6216 West 66th Place, Chicago 38, Ill.

NACE Member **T. J. V. Cudbird** has been named manager of a new anti-corrosion division of Canadian Hanson & Van Winkle Co., Ltd., 2 Silver Ave., Toronto, Ontario, Canada.

John R. Daesen has been appointed technical director of the American Hot Dip Galvanizers Association, Inc., 5225 Manning Place, N.W., Washington 16, D.C. **Charles E. Perry** is the new secretary-treasurer of the association, which recently moved its office from Pittsburgh to Washington, D.C.

William J. Hegerty has been elected to a two-year term on the board of directors of the American Association of Cost Engineers. He is executive vice president of the Colonial Iron Works Co., 17643 St. Clair Ave., Cleveland 10, Ohio.

Thomas F. Humphrey has been appointed to the newly created position of vice president and general manager for Temptron, Inc., Reseda, Cal.

E. A. March has been promoted to director of technology for Crucible Steel Company of America, Pittsburgh 22, Pa.

NACE NEWS

Buffalo Conference Program Revisions Are Made

Technical Program Changes Are Listed For Seven Symposia

Corrections and final changes are given below for the technical program of the 17th Annual NACE Conference to be held March 13-17 in Buffalo, N.Y. These changes have been made since the Advance Program was published on Pages 45-55 of the January issue of CORROSION.

Refining Industry, Session, given on Page 47 of the January issue: David B. Boies' company affiliation has been changed to Armour Research Foundation, Chicago, Ill.

Protective Coatings, Session Two, given on Page 48 of January issue: a fourth author (D. L. Andersen) has been added to the paper by Harold Wittcoff, Don E. Floyd and David W. Glaser.

Corrosion Principles, given on Page 50 of January issue: A. H. Roebuck of Westco Research, Fort Worth, Texas, has changed the title of his paper to "Corrosion Products—Their Effect on Corrosion Rates." Also, the paper by E. H. Phelps has been changed as follows: Effect of Solution pH on Mechanism of Stress Corrosion Cracking of a Martensitic Stainless Steel," by H. J. Bhatt and E. H. Phelps, U. S. Steel Corp., Monroeville, Pa.

Inhibitors, Session Two, given on Page 50 of the January issue: Two titles have been added. Heat Transfer Testing of Cooling Water Treatments—Part 1: Laboratory Evaluation, by A. J. Freedman, W. J. Ryzner and J. D. Knapp, Nalco Chemical Co., Chicago, Ill. Part 2: Field Evaluation, by B. J. Northan, G. Reid and P. R. Puckorius, Nalco Chemical Co., Chicago, Ill.

General Corrosion, given on Page 50 of the January issue: A title has been added for the paper to be given by Bernard Husock as part of the panel discussion: Use of Pipe-to-Soil Potential in Analyzing Underground Corrosion Problems.

Elevated Temperature, Session Two, given on Page 52 of January issue: Title of the paper by A. Moskowitz and L. Redmerski has been changed to "Corrosion of Superalloys at High Temperatures in the Presence of Contaminating Salts." And the paper by W. R. Wardrop and F. H. Humphrey has been changed

DEATHS

James Campbell Everett, secretary of the Detroit Section, died November 20. He was general sales manager of Truscon Laboratories and had been a member of NACE since 1956. He was a graduate of the University of Michigan.

to "A New Design for Reinforced Plastic Tanks."

Cathodic Protection, Session Two, given on Page 54 of January issue: Title change and addition of a second author have been made on the paper by H. S. Preiser as follows: Electrochemical Approach to Cavitation Damage and Its Prevention, by H. S. Preiser, Bureau of Ships, Washington, D. C., and B. H. Tytell, Boston Naval Shipyard, Boston, Mass.

North Central Region

1961 St. Louis Conference Symposia Chairmen Named

Symposia chairmen have been appointed for the 1961 North Central Region Conference to be held October 9-11 in St. Louis, Mo. They are listed below: Protective Coatings, Inorganic: C. J. O'Boyle of Metco, Inc., Chicago, Ill., Utilities: Ray Kern of Union Electric Co., St. Louis, Mo., High Temperature Metals: H. J. Siegel of McDonnel Aircraft Corp., St. Louis, Mo., Brewing Industry: C. L. Griffin of Anheuser-Busch, Inc., St. Louis, Mo., Petroleum Refining Industry: W. A. Heideman of Socony Mobil Co., Inc., East St. Louis, Ill., Transportation Industry: Louis Shaywitz of Transportation Materiel Command, St. Louis, Mo., Non-Metallics: J. F. Revilock of National Carbon Co., Cleveland, Ohio, Protective Coatings, Organic: S. L. Lopata of Carboline Company, St. Louis, Mo., Metals for the Process Industry: H. O. Nordquist of Joseph T. Ryerson & Sons, Inc., St. Louis, Mo., and Sheet Linings: G. P. Kern of Garlock, Inc., Camden, N.J.

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Greater St. Louis Section officers for 1961 are Chairman A. O. Fischer, Vice Chairman M. S. VanDevanter, Secretary W. T. Woodson and Treasurer Louis Shaywitz.

Cleveland Section saw movies from the National Aeronautics and Space Administration at its December 20 meeting.

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Kansas City Section heard NACE Executive Secretary T. J. Hull speak on "The NACE Past, Present and Future" at the January 9 meeting.

At the December 12 meeting, the section unanimously selected R. H. Goodnight of Cooks Paint Company as general chairman for the 1962 NACE Annual Conference to be held in Kansas City, Mo.

●

Detroit Section heard R. W. Flournoy of Reynolds Metal Co., Richmond, Va., speak on aluminum alloys for chemical resistance at the November 17 meeting.

The 1961 North Central Region Conference will be October 9-11, Chase Park Plaza Hotel, St. Louis, Missouri.

All Booth Spaces Assigned for 1961 Corrosion Show

All booth space has been assigned for the 1961 Corrosion Show to be held in conjunction with the 17th Annual NACE Conference in Buffalo, N. Y., March 13-17. The new exhibitors listed below are late additions to the list published on Page 55 of the January issue of CORROSION.

The new exhibitors include Allied Chemical Corporation's Plastics Division, Bishopric Products Company, Krylon, Inc., Detroit Graphite Company, Chicago Bridge & Iron Company and Tex-Tube, Inc.

Page 55 of the January issue included a list of the exhibitors by booth numbers and a partial list of products to be exhibited.

The 1961 Corrosion Show will be open from 10 am to 5 pm on March 14-16 and will be open to all conference registrants. Other persons interested in visiting the Corrosion Show only can obtain guest invitations at the conference registration desk.

All conference activities and the Corrosion Show will be held in the Hotel Statler-Hilton.

Canadian Region

Montreal Section has scheduled Alfred P. Knapp of Knapp Mills Inc., Long Island City, N. Y., to be guest speaker for the February 14 meeting. His subject will be "Uses of Lead-Bonded Steel and Insmetal in Corrosion Resistant Equipment."

For the March 14 meeting, a paper is to be given on corrosion problems confronted by a consulting engineer.

New section officers are Chairman W. A. Mueller, Vice Chairman N. D. Woollings, Secretary-Treasurer P. H. Tolcher, Program Chairman D. M. Derworiz, Publicity Chairman J. E. Sheppard and Trustee H. A. Hencher.

Southeast Region

Tidewater Section heard John W. Berryman, Jr., Fifth Naval District, Norfolk, Va., talk on control of corrosion by cathodic protection at the December 7 meeting. Next section meeting is scheduled for April 12.

New section officers elected recently are Chairman John W. Berryman, Jr., Vice Chairman Edward E. Gross of Norfolk Redevelopment and Housing Authority, Norfolk, Va., and Secretary-Treasurer William D. Lyliston of Newport News Shipbuilding and Drydock Co., Newport News, Va.

South Central Region

HOUSTON SECTION held its annual ladies night meeting December 13. Shown above shaking hands are O. A. Melvin, new section chairman of Carboline Co., and guest speaker Chester H. Lauck of Continental Oil Co., better known as Lum of the radio and movie team of Lum and Abner. Also shown is A. C. Flory of Mavor-Kelly, Houston, past program chairman. In photograph at right is shown the new section officers during a planning session. From left to right they are W. A. Wood, Jr., alternate Engineering Council representative; R. M. Robinson, program committee; John Wilson, entertainment and funds; J. T. Payton (standing), Trustee; O. A. Melvin, chairman; Benton Russell, vice chairman; and W. M. Koehler, secretary-treasurer.

Carpenter and Thorn to Be South Central Chairmen

Dan H. Carpenter of Atlas Powder Company, Oklahoma City, Okla., has been elected 1961 chairman of the South Central Region. He has been vice chairman of the region for the past year and has served as past chairman and trustee for the Central Oklahoma Section, general arrangements chairman for the 1957 South Central Region Conference and assistant secretary-treasurer for the region.

Carpenter

Other regional officers elected are Vice Chairman Carl M. Thorn, Secretary-Treasurer W. C. Koger and Assistant Secretary-Treasurer C. L. Woody.

Shreveport Section completed plans for its February 14-15 short course to be held at Centenary College. Registration fee will be $15. The two-day sessions will include discussions on fundamentals of corrosion, economics, cathodic protection, coatings and specialized corrosion problems.

Frank Therrell, Jr., of Interstate Oil Pipe Line Company spoke on the economics of cathodic protection at the January 3 meeting. Thirty guests and members attended. W. E. Moore was elected section treasurer to replace T. M. Davis, who resigned because of his transfer from the city.

Central Oklahoma Section heard John Y. Lomax of Hercules Powder Company speak at the Jan. 9 meeting on uses of Penton chlorinated polyether as a chemical resistant coating and lining.

Officers for 1961 elected at the December 12 meeting are Chairman Truel Adams of Arkansas Louisiana Gas Co., Vice Chairman John Knox of Halliburton Company, Secretary-Treasurer Elmer L. Curry of Cities Service Gas Co., and Trustee Frank Burns of General Asphalt Company. Guest speaker was Cecil Gibson of Oklahoma Natural Gas Co., who spoke on improving a corrosion control program through training.

West Kansas Section installed the following 1961 officers at its January 5 meeting: Chairman Robert E. Adams of Mobile Oil Co., Clafing, Kan., Vice Chairman Robert O. Faris of National Cooperative Refinery Association, Great Bend, Kan., and Secretary-Treasurer T. J. Gordon of Halliburton Co., Great Bend, Kan.

Permian Basin Section heard Glen Roberson of Standard Oil Company of Texas speak on development of a corrosion control program for the Puckett Field at the January 10 meeting attended by 50 members and guests.

Next meetings are scheduled for February 14 and March 14.

North Texas Section scheduled a talk on effective communication by R. L. Switzer of Atlantic Refining Company for the January 9 meeting. Results of the 1961 officer election were made as follows: Chairman Jerry R. McIntyre, Vice Chairman George F. Hunt, Secretary-Treasurer Tony Prasil and Trustee Morris Bock.

The 1961 South Central Region Conference and Exhibition will be October 24-27, Shamrock-Hilton Hotel, Houston, Texas.

Complete Program Is Listed for St. Louis Corrosion Short Course

Final program is given below for the Short Course in Corrosion sponsored by the University College and the School of Engineering of Washington University at St. Louis, Mo., with the cooperation of NACE. The short course will be held June 5-9.

Two concurrent lectures on fundamentals of corrosion control are included for the June 5 sessions. One lecture is to cover the basic fundamentals for those persons just starting in corrosion control work or for persons wishing to obtain a refresher in corrosion fundamentals. The second series of lectures will cover the more advanced theories for persons who are specifically interested and concerned with this advanced work.

Monday, June 5

Corrosion Theory and Mechanisms— Basic Considerations: (1) Corrosion Theories and (2) Types of Corrosion, by L. E. Stout, Washington University, St. Louis, Mo.

Corrosion Theory and Mechanisms— Advanced Considerations: (1) Solid State Theory of Corrosion-Metallurgical Aspects by L. B. Gulbransen, Washington University, St. Louis, Mo., and (2) Role of Pressure of Behavior of Metal-Oxygen Corrosion and Oxidation, by J. N. Ong, Washington University, St. Louis, Mo.

Corrosion Testing: (1) Fundamental Studies Using Potentiostatic and Galvanostatic Techniques, by Norman Hackerman, University of Texas, Austin, Texas, and (2) Empirical Techniques: Laboratory Testing With Attention to Duplicating Field Conditions; Field Testing and Evaluation, by A. O. Fisher, Monsanto Chemical Co., St. Louis, Mo.

Tuesday, June 6

Corrosion Control and Preventive Methods: (1) Anodic Passivation (Anatrol) and (2) Cathodic Protection, by J. D. Sudbury, Continental Oil Co., Ponca City, Okla.

Corrosion Control and Preventive Methods: (1) Theory and Application of Inhibitors, by G. S. Gardner, Amchem Products Inc., Ambler, Pa., and (2) Process Control and Change, by O. H. Fenner, Monsanto Chemical Co., St. Louis, Mo.

Wednesday, June 7

Corrosion Resistance and Application of the Newer Metals: (1) Titanium and Its Alloys and (2) Zirconium and Its Alloys, by W. G. Renshaw, Allegheny Ludlum Steel Corp., Pittsburgh, Pa.

Corrosion Resistance and Application of Steel and Low Alloy Steels, by C. P. Larrabee, U. S. Steel Corp., Monroeville, Pa.

Corrosion Resistance and Application of Copper and Copper Base Alloys, by A. W. Tracy, American Brass Co., Waterbury, Conn.

Corrosion Resistance and Application of the Light Metals, by E. D. Verink, Jr., Aluminum Company of America, Pittsburgh, Pa.

Thursday, June 8

Corrosion Resistance and Application of the Stainless Steels: (1) Ferritic and Martensitic Stainless Steels, Wrought and Cast and (2) Austenitic Stainless Steels, Wrought and Cast, by W. A. Luce, Duriron Company, Dayton, Ohio.

Corrosion Resistance and Application of Nickel and Nickel Base Alloys; Corrosion Resistance and Application of Special Alloys, by E. G. Holmberg, International Nickel Co., Inc., New York City, N.Y.

Friday, June 9

Fundamental Concepts in Formulation and Use of Synthetic Polymers: (1) Rigid Plastics, (2) Thermosetting Resins, (3) Thermoplastic Resins and (4) Elastomeric Compounds, by H. J. Lanson, U.S. Vehicle and Chemical Co., St. Louis, Mo.

Protective Coatings: (1) Organic Coatings and (2) Metallic and Metallo-Organic Coatings, Including Refractories, Plasma Jet, etc., by W. B. Meyer and W. T. Woodson, St. Louis Metallizing Co., St. Louis, Mo.

Five NACE Short Courses Set for First Half of 1961

Five corrosion control short courses have been scheduled for 1961 in which NACE is participating. They are listed below.

The first short course has just been held: the Houston Section's 7th annual Corrosion Control Short Course. A record breaking attendance is expected.

Another short course is scheduled this month also: the Shreveport Section Corrosion Short Course, to be held February 14-15 at Centenary College, Shreveport, La.

The other three short courses are scheduled for June. They are the Washington University Short Course co-sponsored by the Greater St. Louis Section on June 5-9 (see accompanying story on this page for detailed program), the 6th Annual Appalachian Underground Corrosion Short Course at the University of West Virginia, Morgantown, June 6-8 and the Greater Boston Section Corrosion Short Course to be held June 20-21 at Wentworth Institute in Boston.

SECTION CALENDAR
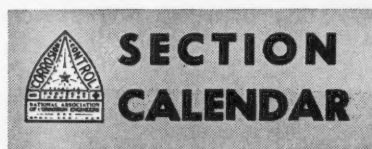
February

1 Schenectady-Albany-Troy Section. "What I'd Like to Know About Corrosion," by D. A. Vermilyea, General Electric Research.
7 Philadelphia Section.
10 Rocky Mountain Section.
13 Kansas City Section.
13 Greater St. Louis Section. Corrosion Resistance Properties and Uses of 17-4 PH Steel, by J. J. Halbig.
13 Central Oklahoma Section.
13 North Texas Section. Torch Restaurant, Dallas
14 San Francisco Bay Area Section.
14 Houston Section.
14 Permian Basin Section.
14 Twin City Section.
14 Montreal Section.
16 Alamo Section.
16 Vancouver Section.
21 Chicago Section. Past Chairmen's night.
21 Greater Boston Section. Biological Influences on Deterioration of Materials in Marine Environments, by Albert P. Richards.
21 Baltimore-Washington Section. Corrosion Problems in Water Handling, by D. W. Auld.
21 Cleveland Section.
27 Tulsa Section.
28 Panhandle Section.
28 Southwestern Ohio Section.

March

1 Schenectady-Albany-Troy Section. Corrosion Problems Associated With Copper Base Alloys, by Wilson Lynes.
13 Kansas City Section.
13 Greater St. Louis Section. Process Industry Corrosion by A. S. Krisher.
13 Central Oklahoma Section.
13 North Texas Section. Torch Restaurant, Dallas, 6:30 pm.
14 San Francisco Bay Area Section.
14 Houston Section.
14 Permian Basin Section.
14 Twin City Section
14 Montreal Section. Corrosion Problems Facing a Consulting Engineer.
16 Vancouver Section.
16 Alamo Section.
21 Chicago Section. Corrosion Contractors Panel Discussion.
21 Kanawha Valley Section. Marietta, Ohio.
27 Tulsa Section.
28 Panhandle Section.
28 Southwestern Ohio Section. Cincinnati, Ohio. Inhibitors and Chemical Treatments for Corrosion Protection, by William D. Gordon.

Facts about pickling acid inhibitors

Nearly 40 years ago Amchem developed the first pickling acid inhibitor —RODINE—and with it revolutionized acid pickling. Only a few of the steel mills of the time believed that the addition of less than one percent RODINE to a sulfuric acid pickling bath could save substantial amounts of acid and metal, while increasing the life of the bath. Today there is no mill chemist who does not know about RODINE and its proven performance in eliminating waste of valuable metal and acid, and its ability to pay for itself through the savings thus gained.

In the past few years much attention has been focused on the use of wetting agents to accelerate pickling. But the fact remains that pickling cycles cannot be reduced by the use of wetting agents alone without severe overpickling problems. Wetting agents do help the acid run off surfaces removed from pickle baths, and, in so doing, reduce carry-over of acid into the rinse.

Wetting agents should not be confused with inhibitors to protect the metal and save acid wasted in pitting it. They should not be expected to miraculously speed the removal of scale, even at the expense of wasting the metal. However, the *proper* combination of *real inhibitor* plus correct wetting agent can have beneficial effects on pickling practices.

Only a true inhibitor such as RODINE can offer steel producers solid advantages in pickling. Baths can be operated longer and less acid is required to keep them at desired concentration. Costs of charging and cleaning the bath are reduced, less handling and storing of acid is required. A RODINE bath produces far fewer rejects —steel emerges with uniformly smooth, bright clean surfaces, free of pits, blisters and smut.

When an Amchem Technical Representative enters your pickle house, you can be assured of experienced assistance in improving your pickling. He will recommend the proper RODINE to 1) prevent needless consumption of acid after scale removal, 2) prevent smutting, pitting and overpickling, 3) produce a stable, free-rinsing foam blanket, 4) improve rinsability and reduce carry-over, and 5) produce a brighter, cleaner surface. Only the Amchem Representative can do this for you because he has at his command the most widely diversified and accepted line of real inhibitors and correct wetting agents available.

NACE Members to Give Papers At London Corrosion Congress

Twenty-one NACE members will be presenting technical papers at the First International Congress on Metallic Corrosion to be held April 10-15 in London, England, at the Imperial College of Science and Technology, South Kensington.

Another NACE member, H. H. Uhlig of Massachusetts Institute of Technology, will give one of the plenary lectures during the congress. His topic will be "The Advancing Frontiers of Corrosion Science."

Papers To Be Given

Papers to be presented by NACE members are listed below:

Atmospheric Corrosion of Steels as Influenced by Chemical Composition, by C. P. Larrabee and S. K. Coburn, U.S. Steel Corp., Monroeville, Pa.

Alternating Current Corrosion, by F. O. Waters, San Diego Utilities Dept., San Diego, Cal.

Corrosion Inhibition and Molecular Structure, by N. Hackerman and R. M. Hurd, University of Texas, Austin, Texas.

Passivity of Nickel and Nickel-Base Alloys, by N. D. Greene, Rensselaer Polytechnic Institute, Troy, N.Y.

Effect of Cooling Rate on Susceptibility of High Strength Aluminum Alloys to Intergranular Corrosion, by W. Beck and S. J. Ketcham (non-member), U. S. Naval Air Materials Center, Philadelphia, Pa.

Accelerated Corrosion Testing of Metals, by W. D. McMaster, General Motors Corp., Warren, Mich.

An Anodic Stress Corrosion Test for Aluminum-Magnesium Alloys, by H. P. Godard and G. G. Booth (non-member), Aluminium Laboratories Ltd., Kingston, Ontario, Canada.

Choice of Zinc Content for Cladding on Aluminum-Zinc Clad Aluminum-Manganese Alloy for Handling Supply Waters, by H. S. Campbell and F. C. Porter, British Non-Ferrous Metals Research Association, London, England.

Anodic Behavior of a Lead-Platinum Bi-Electrode in Chloride Electrolyte, by L. Shrier and E. Littauer (non-member), Battersea College of Technology, London, England.

Effect of Nickel Content on Resistance to Stress Corrosion Cracking of Iron-Nickel-Chromium Alloys in Chloride Solutions, by H. R. Copson, International Nickel Co., Inc., Bayonne, N.J.

Effect of Composition and Structure of Stainless Steels On Resistance to Stress Corrosion, by E. H. Phelps and R. B. Mears, U.S. Steel Corp., Monroeville, Pa.

Corrosion of Condenser Tubes Under Conditions of Local High Temperature, by C. Breckon and P. T. Gilbert, Yorkshire Imperial Metals Ltd., Leeds, England.

Laboratory Hot Spot Corrosion Tests of Condenser Tube Alloys at Hot Spots, by H. S. Campbell and R. S. Bem (non-member), British Non-Ferrous Metals Research Association, London, England.

Some Unusual Corrosion Problems in the Chemical Process Industries, by M. G. Fontana, Ohio State University, Columbus, Ohio.

Corrosion in Oil Refinery Equipment,

by H. G. Geerlings and J. C. Jongebreur (non-member), N. V. Bataafsche Petroleum MIJ, Hague, Holland.

Future Corrosion Research on Ferrous Metals, by J. C. Hudson, British Iron and Steel Research Association, London, England.

Proceedings To Be Published

Proceedings of the congress, including all scientific papers presented, will be published after the meeting by Butterworths, 88 Kingsway, London, W.C.2, England.

Greco to Speak at Two Corrosion Short Courses

NACE President-elect Edward C. Greco of United Gas Corp., Shreveport, La., has accepted invitations to speak at two corrosion control short courses in which NACE participates.

Mr. Greco will give the keynote address at the Sixth Annual Appalachian Underground Corrosion Short Course to be held June 6-8 at the University of West Virginia, Morgantown. This short course is sponsored by the university and is endorsed by NACE and the American Water Works Association.

Mr. Greco also will speak before the Shreveport Section's Corrosion Control Short Course to be held February 14-15 at Centenary College.

Northeast Region

Boston Section Selects Short Course Chairmen

Committee chairmen have been selected for the Greater Boston Section Short Course to be held June 20-22 at Wentworth Institute. Committee chairman will be W. S. Sanders of Algonquin Gas Transmission Company. Other chairmen and committee members are listed below:

Program: Chairman Joseph R. Sarnosky of Westinghouse Electric Co., Kenneth E. Sawyer of Western Union Telegraph Co., and Charles Mettam of Esso Standard Oil Company.

Registration: Chairman Kenneth E. Gibbons of Chase & Sons, Inc., B. F. Barnwall of Lithecote Co., and Carlton L. Goodwin of Portland Pipe Line Corporation.

Publicity: Chairman Joseph D. Buckley of Buckley Iron Works, Inc., Walter E. Langlois of Westinghouse and Steve Stephenus of Chase & Sons, Inc.

Pittsburgh Section heard J. M. Williams of Avco Corporation speak on corrosion in nuclear fields at the January 5 meeting.

Philadelphia Section had N. D. Greene of Rensselaer Polytechnic Institute speak on metallic passivity based on concept of mixed potentials and the results of potentiostatic polarization measurements at the December 20 meeting. Sixty-three members and guests were present.

Officers for 1961 were elected as follows: Chairman Douglas F. Wooley, Jr., of Pennsalt Chemical Co., Vice Chairman Richard K. Kichline of RKL Controls, Inc., and Secretary-Treasurer Walter Lee Sheppard, Jr., of Electro Chemical Engineering & Manufacturing Co.

Section meetings are scheduled for February 7 and May 31.

Kanawha Valley Section had two guest speakers for the January 3 meeting. M. E. Carlisle of Aluminum Company of America spoke on aluminum pipe for pipelines and industrial plant use. W. J. Immel of Tennessee Gas Transmission Company spoke on cathodic protection for plant yards using distributed anode groundbeds.

Metropolitan New York Section had 63 members and guests at its annual Christmas meeting held December 14. NACE President George Best made an informal talk on the association. Officers elected at the meeting were Chairman S. N. Palica, Vice Chairman R. E. Backenbach and Secretary-Treasurer G. W. Kurr.

R. H. Barton of du Pont was scheduled guest speaker for the January 18 meeting. His subject was rubber and elastomers.

Greater Boston Section had 41 members and guests attending the December 21 meeting despite a heavy snowstorm. Guest speaker was Melvin Romanoff of the National Bureau of Standards, who spoke on underground corrosion of metallic structures.

Western Region

E. F. Bladholm Elected Western Region Director

E. F. Bladholm of Southern California Edison Co., Los Angeles, Cal., has been elected director for the Western Region. An active NACE member, he was 1959 chairman of the Western Region. He has been involved in corrosion control work with pumps and power plants since 1932.

Other new officers elected for the Western Region are Chairman O. L. Hudrlik of Molalla, Ore., Vice Chairman F. O. Waters of San Diego Utilities Department, La Mesa, Cal., and Secretary-Treasurer Sam Grubb of Portco Corp., Vancouver, Wash.

Bladholm

San Francisco Bay Area Section had Harold C. Templeton of Alloy Steel Products Co., Inc., as guest speaker for the January 10 meeting. He spoke on cast austenitic stainless steels.

Portland Section had James F. Norton speak on corrosion fundamentals for the January 12 program.

Protective coatings for the petroleum industry were discussed by Willard F. Kerlinger at the December 8 meeting. The 1961 section officers also were introduced. They are Chairman George Merz, Vice Chairman Keene Shogren and Secretary-Treasurer Robert Best.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1961

March 12—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.

March 13-17—17th Annual Conference and 1961 Corrosion Show, Buffalo, N. Y., Hotel Statler.

March 17—NACE Board of Director's Meeting, Hotel Statler, Buffalo, N. Y.

Oct. 4-6—Western Region Conference, Hotel Multnomah, Portland, Oregon.

Oct. 9-11—North Central Region Conference, St. Louis, Chase Park Plaza Hotel.

Oct. 24-27—South Central Region Conference and Exhibition, Shamrock-Hilton Hotel, Houston.

Oct. 30-Nov. 2—Northeast Region Conference, New York City, Hotel Statler.

Southeast Region Conference, Miami, Fla., in conjunction with Miami Section's short course.

1962

March 19-23—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 1-4—Northeast Region Conference, Hotel Sheraton Ten Eyck, Albany, N. Y.

October 9-11—North Central Region Conference.

October 11-12—Southeast Region Conference, Birmingham, Ala.

October 16-19—South Central Region Conference and Exhibition, Granada Hotel, San Antonio.

1963

March 18-22—19th Annual Conference and 1963 Corrosion Show. Convention Hall, Atlantic City, N. J.

October 14-17—South Central Region Conference, Oklahoma City, Okla.

SHORT COURSES

1961

February 2-3—7th Annual Houston Section Corrosion Control Short Course, Rice Hotel, Houston, Texas.

February 14-15—Shreveport Section Corrosion Short Course, Centenary College, Shreveport, La.

June 5-9—Corrosion Short Course, co-sponsored by NACE Greater St. Louis Section and Washington University, to be held at Washington University, St. Louis.

June 6-8—6th Annual Appalachian Underground Corrosion Short Course, University of West Virginia, Morgantown.

June 20-21—Greater Boston Section Corrosion Short Course, Wentworth Institute, Boston, Mass.

4. CORROSIVE ENVIRONMENTS

4.6 Water and Steam

4.6.2, 6.3.20, 8.4.5

Effects of Local Boiling on Corrosion and Crud Deposition of Zircaloy Surfaces. R. T. Esper, W. E. Hopkins, Jr., C. Jacklin and J. H. Phillips. Paper before Am. Power Conf., Chicago, March 26-28, 1958. Proc. Am. Power Conf., **20,** 697-708 (1958).

Tests on surface effects of nucleate boiling program were conducted with conditions of various time intervals, water velocities and heat fluxes. Metallographic and chemical descaling data showed slightly more material deposited on boiling specimens than on nonboiling specimens. This slight difference in deposition was not considered significant in view of the small amount of deposition encountered on both specimens. Presence of boiling did not affect corrosion rate of Zircaloy-2 in these tests. Results of 4 tests tend to indicate that velocity affects surface deposition under nucleate boiling as well as nonboiling conditions. For comparable exposure period under same test conditions specimens at lower velocity retained a heavier deposit than those at a higher velocity. There appeared to be no pits, metal cracking, or other changes on specimen surfaces as a result of exposure to boiling condition. Tables, diagrams.—INCO. 18751

4.6.1, 3.4.7, 6.3.20, 6.2.3, 6.2.5

Corrosion of Zirconium, Carbon Steel and Stainless Steel in High Temperature Water. R. J. Lobsinger. General Electric Co. Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-56995, August 6, 1958, 11 pp. Available from Office of Technical Services, Washington 25, D. C.

Corrosion data obtained on zirconium, carbon steel, and stainless steel exposed to high-temperature water at pH values from 7.0 to 10.0 are reported. Tests were conducted to support existing data and to determine the important variables in each system.—NSA. 18882

4.6.2, 6.2.2, 6.2.3

Oxidation Rate of Steel and Cast Iron in a Steam Atmosphere. (In English.) P. Szeki. Acta Technica, **22,** No. 1-2, 129-134 (1958).

Based on experiments with cast iron (3.28 per cent carbon, 0.33 percent manganese, 1.74 per cent silicon, 0.10 per cent sulfur, 0.29 per cent phosphorus) exposed to a steam atmosphere at 750 C and with mild low-carbon steel (0.11 carbon, 0.39 manganese, 0.23 silicon, 0.031 sulfur, 0.031 phosphorus) in steam at 650 C; formulas for the oxidation rate constant are found for each of both materials thought useful in oxide coating. 7 references.—MR. 18972

4.7 Molten Metals and Fused Compounds

4.7, 6.2.5, 6.3.10

Preliminary Investigation of Corrosion by Molten Sodium Hydroxide Flowing in Tubes of AISI 347 Stainless Steel, Inconel, and Nickel Having Average Outer-Wall Temperatures of 1500 F (815 C) and a Circumferential Temperature Gradient of 20 F (11 C). Don R. Mosher and Leland G. Desmon. U. S. National Advisory Cttee. Aeronautics, Research Memo, E51J16, 1952 (Declassified 1958), 20 pp.

These materials were tested for dynamic corrosion at a velocity of 15 ft/sec at 1500 F (815 C). All containers were preferentially attacked.—MA. 18878

4.7, 6.3.10, 2.3.8

Progress Report on Volatility Pilot Plant Corrosion Problems to April 21, 1957. L. R. Trotter and E. E. Hoffman. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2495, October 17, 1958, 41 pp. Available from Office of Technical Services, Washington, D. C.

Many complex corrosion problems have been encountered in the preliminary bench tests and early operation of the Fused-Fluoride Volatility Process. Several of the problems have been investigated and are fairly well understood, such as embrittlement of nickel by sulfur-containing fluoride salts and the heavy attack on even the most promising structural materials by fused fluoride salts in the presence of air contamination at elevated temperatures. The heavy attack encountered on nickel rods in the fluorination vessel during early test runs is not completely understood, although it is believed that improved handling techniques and maintenance of a gas-tight system will reduce the attack. This report merely serves to emphasize that in a complicated high-temperature system of this type there are many material and design problems which must be solved before reliable long-time operation can be assured. (auth.)—NSA. 18977

4.7, 6.2.1

Hot-Dip Aluminum Coating on Steel. Rept. 6. The Reaction of Solid Iron with Molten Aluminum. (In Japanese.) Masayoshi Tagaya, Shigeteru Isa and Yoshio Tani. J. Metal Finishing Soc., Japan, **10,** No. 10, 363-368 (1959) Oct.

Mutual diffusion of molten aluminum in solid steels was studied. 10 mm diameter holes were bored in the center of 16 mmϕ $\times$ 15 mm cylindrical steel specimens (0.02, 0.11, 0.45, 0.83% carbon steel, 2% chromium-1% molybdenum steel, 13 chromium and 18-8 stainless steel), into which various aluminum alloy rods (99.99% aluminum, 98 aluminum, 98% aluminum + 5% silicon and 98% aluminum + 5% silicon + 0.2% beryllium) with nearly the same diameter as the hole were tightly inserted. These combined specimens were heated in vacuum at 680, 720, 760 and 800 C for 6 hrs., then cooled, and the phenomena of mutual diffusion between the molten aluminum alloys and the solid steels was investigated.

99.99% aluminum and 98% aluminum, diffuse deepest into every steel and the lower the carbon in steel, the deeper is the iron-aluminum alloy layer into the steel. In the case of molten aluminum + silicon and aluminum + silicon + beryllium, silicon and beryllium inhibit diffusion of aluminum into steel; lumps of iron-aluminum alloy are noticeable in aluminum and considerable dissolution of iron into molten aluminum is also found.

In general, the diffusion constant of 98% aluminum is larger than that of other aluminum alloys while the minimum diffusion is reached with aluminum + silicon + beryllium alloy. Activation energy increases rapidly with increase of carbon content (within the range 0.02 to 0.11%) but is nearly constant upon further increase. With 99.99% aluminum and 98% aluminum, the activation energy is about 40,000 cal/mol, with aluminum + silicon alloy about 20,000 cal/mol and with aluminum + silicon + beryllium alloy much smaller.

This investigation confirmed the inhibiting action of silicon and beryllium on the diffusion of aluminum into steel but showed also that silicon or beryllium accelerates the dissolution of iron into molten aluminum bath.   18623

4.7, 8.4.5

Material and Corrosion Problems in the Reactor with Liquid Metals as Coolant. (In German.) Willibald Machu. Cairo Univ. Atomkern-Energie, **3**, 141-144 (1958) April.

Last part in a series on material and corrosion problems in liquid metal cooled reactors is presented. The behavior of reactor materials in liquid bismuth, lead and mercury is described. The corrosion mechanism of liquid metals is briefly discussed.—NSA. 18886

4.7, 8.4.5

Material and Corrosion Problems in a Reactor with Liquid Metals as Coolant. (In German.) Willibald Machu. Cairo Univ. Atomkern-Energie, **3**, 97-100 (1958) March.

First part of a series on material and corrosion problems in a liquid metal cooled reactor is presented. The behavior of different materials in liquid sodium and calcium is discussed.—NSA. 18885

4.7, 6.2.2, 3.7.2

Attack of Titanium-Bearing Iron by Molten Zinc Saturated with Iron. Dietrich Horstmann. Arch. Eisenhüttenw., **29**, No. 12, 731-735 (1958).

Alloys with up to 5% titanium and 0.03% carbon were cast into square specimens and immersed in molten zinc. As with soft iron, at high and low temperatures, the weight loss varies parabolically with time; around 500 C the relation is linear. The effect of titanium is to increase the temperature range of linear attack, particularly at the low-temperature end; the deviation from the parabolic law starts at 450 C in an alloy with approximately 5% titanium. In the temperature ranges where the attack is parabolic, the severity of attack is determined by diffusion within the Γ-layer. —MA.   18778

18a

4.7, 3.7.3, 6.3.10, 6.3.11

An Evaluation of the Corrosion and Oxidation Resistance of High-Temperature Brazing Alloys. Period covered: July 1954-September 1955. E. E. Hoffman, P. Patriarca, C. F. Leitten, Jr. and G. M. Slaughter. Oak Ridge National Lab., U. S. Atomic Energy Commission Pubn., ORNL-1934, November 7, 1956 (Declassified October 9, 1959), 40 pp. Available from Office of Technical Services, Washington, D. C.

Many of the brazing alloys which were investigated were highly promising for sodium-to-air radiator service. Alloy systems of nickel-silicon-boron, nickel-chromium-silicon-boron and nickel-chromium-silicon were especially favorable. Precious-metal alloys were, in general, severely attacked by sodium, as were many of the silicon-free, chromium-free, phosphorus-bearing alloys. Alloys containing manganese, tin, or copper exhibited poor resistance to oxidation at 1500 F. In most cases, oxidation was more pronounced at 1700 F. For fused-fluoride-to-sodium heat exchanger service, the alloy systems nickel-chromium-phosphorus, nickel-chromium-silicon-boron, nickel-silicon-boron and nickel-germanium-chromium-silicon show promising corrosion resistance. Although the nickel-chromium-silicon alloy was compatible with sodium, it was severely attacked by the fluoride bath. The binary alloy 88 nickel-12 phosphorus (alloy A-10) was incompatible with sodium but possessed good resistance to fluoride attack. Tests seem to indicate that complex alloy systems containing varying percentages of silicon and phosphorus as minor constituents may be compatible with both sodium and the fused salts, whereas the binary alloys exhibited compatibility with only one of these testing media. The only brazing alloys found to be compatible with fused sodium hydroxide were precious-metal alloys such as 82 gold-18 nickel. In evaluating the corrosion and the oxidation resistances of a brazing alloy for a specific application, emphasis was placed on the seesaw-corrosion and cyclic-oxidation studies, since these tests more nearly simulate the expected operating conditions than do the static tests. It must be remembered, however, that before a brazing alloy is selected for a given operation it should be tested further under the conditions which would closely simulate service conditions. (auth.)—NSA.   19209

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5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.4

The Hot-Dip Galvanized Coating and Corrosion Resistance. Pts. I & II. J. H. Nicholls. Corrosion Technology, **6**, Nos. 9, 10, 275-276, 284; 307-309 (1959) Sept., Oct.

Position of zinc relative to other commonly used metals for protective coatings on steel is briefly compared. Corrosion of galvanizing is discussed in following categories: immersed corrosion (H_2-evolution type and O_2-absorption type), underground corrosion (aerobic or anaerobic) and atmospheric corrosion. Anode corrosion experiments and effects of micro-organisms are reviewed. Classifications of atmospheres and factors of moisture, humidity and atmospheric pollution are considered. Coating life experiments with hot-dip

galvanized coatings in various atmospheres are summarized. Corrosive action of building materials (e.g., wet Portland cement), contact corrosion, and formation of white rust on zinc surface are topics covered. Surface treatment, primers and application of paint to galvanizing is described. Tables, photomicrographs, 23 references.—INCO.   19357

5.3.4, 3.5.9

Observations on the Process of Nickel Deposition by Thermal Decomposition of Nickel Carbonyl at Low Pressures. Pt. III. L. W. Owen. Metallurgia, **59**, No. 356, 295-300 (1959).

Owen obtained good-quality coatings by the decomposition of $Ni(CO)_4$. While the rate of flow of $Ni(CO)_4$ vapor and pressure appeared not to be critical factors, temperature was, the optimum being 210-230 C. Below this range various defects were found in the coating accompanied by a low deposition-efficiency, and above it black powdery deposits were formed. These were inhibited by the addition of CO as a diluent. The range of properties of the coating was considerable, while coating thickness was generally uniform. 18 references.—MA.   19378

5.3.4

Observations on the Process of Nickel Deposition by Thermal Decomposition of Nickel Carbonyl at Low Pressures. Pts. I, II. L. W. Owen. Metallurgia, **59**, Nos. 354, 355, 165-173, 227-233 (1959) April, May.

Pt. I. Properties of the coatings obtained and details of variables controlling the process are given, such as appearance, ductility, microhardness, microstructure, etc. The adhesion and porosity of the coating on various metallic bases are assessed, as well as thickness and shapes. Also mentioned are temperature, pressure, rate of flow, and vapor composition. An attempt is made to relate these factors with each other and the properties of the coating.

Pt. II. Owen gives details of appearance, microstructure, microhardness and ductility and discusses the decomposition process and black-powder formation as well as the vapor movement in the bell jar.—MA.   19377

5.3.4, 5.3.2, 5.2.2

Possibilities of Zinc in the Fight Against Marine Corrosion. (In French.) R. Souské. Corrosion et Anticorrosion, **7**, No. 10, 356-359; disc., 359 (1959) Oct.

Protection of exposed steel by Zn anodes and by Zn plating, spraying, diffusion and painting is reviewed. Salt-spray-test results showing the effects of temperature and Zn purity in hot galvanizing are illustrated.—MA.   19466

5.3.2

Metallic Protective Coats. (In German.) H. Reiniger. Werkstoffe u. Korrosion, **10**, 477-489 (1959) Aug.

Use of sprayed layers of aluminum, zinc, cadmium and lead as corrosion resisting coatings. Uniformity in thickness can be achieved only by mechanical spraying. Coating thickness and spray losses are dependent on the sprayed surface area.—RML.   19448

5.3.4

The Thermal-Oxidation Properties of Metallic Coatings. R. L. Samuel. Product Finishing, **12**, No. 2, 73-86 (1959).

These properties are discussed with reference to Zn, Si, Al, and Cr diffusion,

and use of facing alloys or cladding, for Fe, Ni, Cu, Ti, W and their alloys. Diffusion coatings may be used with advantage instead of expensive materials to obtain improved performance. 12 references.—MA.   19508

5.3.4
Vapour-Phase Plating with Molybdenum and Tungsten. H. W. Schultze. Metal Progress, **76**, No. 3, 74-80 (1959).

Deposits of metals or their refractory compounds are produced by thermal decomposition of the carbonyl or by H reduction of the chloride at temperatures below the m.p. of the metals. Adherent coatings can be produced on ceramics, glass, refractories and graphite. Applications for electrical uses are described.—MA.   19500

5.3.4
Protection Against Corrosion by Means of Metal Layers. (In Dutch.) T. van der Klis. Bedrijf en Techniek, **14e**, No. 340, 634 + 3 pp. (1959) Sept. 19.

A survey of the methods used in producing metal layers of aluminum, cadmium, chromium, gold, indium, cobalt, copper, lead, molybdenum, nickel, platinum, rhodium, silicon, tin, silver, and zinc by means of immersion baths, electrolysis, vapor-plating, deposition by vaporization in a vacuum and other processes.—BTR.   19546

5.3.4
Progress in the Development of a Non-Embrittling Cadmium Electroplating Process. Pt. I. P. N. Vlannes, S. W. Strauss and B. F. Brown. Plating, **46**, No. 5, 467-468 (1959).

The embrittling effect of cadmium is estimated by the angle of bend at which fracture occurs in a plated specimen or the reduction in area in a plated tensile specimen. Cyanide baths appear more embrittling than these containing other complexing agents.—MA.   19545

5.4 Non-Metallic Coatings and Paints

5.4.5, 5.9.4
On the Adhesive of the Organic Film to the Anodized Surface. (In Japanese.) Matsuhei Kishi. J. Metal Finishing Soc., Japan, **10**, No. 4, 7-11 (1959) April.

To find out the difference between the adhesive property of electroplating and of organic coating to metal surface, the acetyl cellulose films as organic are coated on the anodized aluminum plates under various anodizing conditions, and each adhesive strength is measured. The results of the measurement are as follows:

1. Adhesive strength of the coating on aluminum plate anodized in phosphoric acid bath at room temperature is several times greater than the others. However, the strength falls with anodizing temperature rise.

2. Coatings on the aluminum plates anodized in sulfuric or oxalic acid bath and etched by sodium hydroxide have almost the same or slightly less adhesive strength as the above.

3. Such tendency of the adhesive property of organic coating is the same as that in the case of electro-plating of anodized aluminum.   17791

5.4.2, 5.9.2
Oxide Adherence and Nickel Flashing in Vitreous Enameling. H. Crystal and G. Bullock. J. Am. Ceram. Soc., **42**, No. 1, 30-39 (1959) Jan.

Attempts to introduce suitable

amounts of iron oxide into enamel and thus promote adherence by coating steel with layer of deposited and active iron were unsuccessful. During course of this work, it was observed that adherence of enamel to steel pickled in nitric acid was extremely good. Present work established necessary presence of optimum amount of oxidation of specimen and correlation between oxide and enamel adherence. Nickel flashing tends to promote adherence of oxides to sheet steel and also promotes enamel adherence. Using nickel flashing under laboratory conditions, it was possible to achieve adherence of commercially acceptable standard for enamels directly applied. Relation exists between iron content of hydrochloric acid pickling bath and deposition in subsequent nickel flashing. Hydrogen absorbed during pickling is also concerned in nickel flashing. Graphs. —INCO.   17769

5.4.5
Epoxy Resins and Their Use in Various Fields of Technology. (In German.) F. Ohl. Seifen, Ole, Fette, Wachse, **84**, No. 3, 72-74 (1958).

A review covering the composition, properties and methods of preparation of epoxy resin laminates and the use of epoxy resin lacquers in the machinery, aircraft, car and electrotechnical industries, for piping and chimneys and in the chemical industries.—RPI.   17502

5.4.5
On the Behavior of Metallic Zinc in Paints. (In German with English Summary.) H. J. Schuster. Werkstoffe u. Korrosion, **10**, No. 8, 490-494 (1959) Aug.

With the aid of a model cell fundamental facts about the behavior of zinc based paints on iron are explained. Investigations show that the corrosion in-

hibiting action of zinc based paints is, in the first place, dependent on the electrochemical interaction between the pigment and the iron base. Of material importance for a permanent protection, however, is the formation of difficultly soluble zinc compounds which reinforce the texture of the film. These reactions are, after cessation of the electrochemical protection, reinforced by superficial oxidation of the zinc. There is a fundamental distinction between galvanizing and protection by zinc paints. 5 figures. —ZDA.   18667

5.4.5, 5.5.2, 5.6.2
High Polymers in Corrosion-Protection. (In French.) A. Bonaldi and L. Jaque. Corrosion et Anticorrosion, **6**, No. 12, 431-436 (1958) Dec.

A review of the properties and application of protective greases, strippable, non-strippable and sprayed plastic coatings, "cocoons," and paints consisting of polymers in an organic-solvent base.— MA.   18840

5.4.2, 6.6.6, 6.7.2
Investigation of High Temperature Resistant Materials. Summary Report No. 2 for November 1, 1957 to October 31, 1958. C. R. Mason and J. D. Walton. Georgia Inst. Tech., 113 pp. Project No. A-212, Contract NOrd-15701. Available from Engineering Experiment Station, Georgia Inst. of Technology, Atlanta.

Preliminary tests were made on the effects of particle size and substrate temperature on the adherence of 3.5 mil flame-spray coatings on mild steel using 85% zirconium dioxide-15% titanium dioxide powder. Two materials were investigated as possible base coats for flame-sprayed aluminum oxide. One material, consisting of a 70% aluminum-30% aluminum oxide mix, provided ex-

cellent room temperature adherence when it was oversprayed with aluminum oxide and resisted spalling after cooling from 1700 C. The other base material, copper, also provided excellent room-temperature adherence when oversprayed with aluminum oxide but spalled severely when cooled from 1500 F. Exploratory work on coatings produced from flame-sprayed titanium dioxide showed excellent room-temperature adherence. The effects of the ratio of thermite mix to throttling agent and the effect of the shrouding material used during ignition were studied in connection with zirconium disilicide. The thermite reaction between aluminum and fused silicon was considered as a possible means of bonding a high silica body. Cermets containing zirconium carbide and titanium carbide were produced by thermite reactions. Investigations on various throttling materials for thermite reactions are presented. The change in free energy for thermite reactions of beryllium with 13 metal oxides was calculated. The general equation for these reactions is: $Be + MO \rightarrow BeO + M +$ Heat. The 13 oxides which were considered were silicon dioxide, chromic oxide, nickel monoxide, tungsten trioxide, molybdenum trioxide, ferric oxide, Co_3O_4, manganous oxide, titanium dioxide, zirconium dioxide, vanadium pentoxide, hafnium dioxide and aluminum oxide. Tests were made on the rocket nozzle test facility to standardize operating procedures. Nozzles fabricated using the thermite reaction between fused silica and aluminum were too weakly bonded to withstand the physical shock of the start cycle on the small rocket test stand. Nozzles fabricated using the zirconium carbide forming thermite reaction melted rapidly when tested on the small rocket motor. Nozzle containing 85% silica-15% graphite, pressed to 17,500 psi, continued to give the best performance of all silica nozzles tested.—NSA.   18860

5.9 Surface Treatment

5.9.2, 6.3.20, 8.4.5
Preparing Zircaloy-2 for Autoclave Testing—The Pickling and Rinsing Process. D. W. Shannon and B. Griggs. General Electric Co., Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-60433, July 1, 1959, 82 pp. Available from Office of Technical Services, Washington, D. C.

A pickling and rinsing process has been developed to prepare the Zircaloy-2 PRTR fuel elements for autoclave corrosion testing. As background for this process the chemical and corrosion properties of Zircaloy-2 and the chemistry of the pickling process are outlined. The facilities, materials of construction, pickling and rinsing procedures are discussed. Laboratory experiments relative to the pickling and rinsing process, materials of construction and several alternative pickling processes are presented. (auth)—NSA.   19463

5.9.3, 5.4.5
Corrosion Protection of Steel Surfaces. (In German.) Alexander Seils and Siegfried Hagn. Industrie-Anzeiger, **81**, 28-31 (1959) Oct. 20.

Blasting is a prerequisite for successful coating. Outstanding properties of synthetic resin coatings as a corrosion deterrent. Coatings for steel surfaces should be chosen with reference to

weather conditions. The application of coatings at temperatures below 10 C and at relative humidities above 75 percent should be avoided. 4 references.—RML.   19460

5.9.2

Pickling and Pickling Agents. (In French.) J. Rousset. Usine nouvelle, **1959**, Numéro spécial, 16-17, 19-21, 23-25, 27, 29, 31.

The mechanical and chemical removal of oxide films, grease, &c. from metal surfaces is surveyed. Procedures and agents for cleaning Cu and its alloys, Ni and its alloys and light alloys are detailed. The removal of deposits of Ag, Cr, and Sn from Cu alloys and of Ni from Cu alloys and steel is also dealt with. Washing and drying are summarized, and the equipment required for all these processes is described, together with materials for its construction. 14 references.—MA.   19493

5.9.1, 6.4.2

Finishing Aluminium. R. Thake. Can. Paint & Var., **33**, No. 9, 38-40, 59-62 (1959).

The article describes methods of cleaning, surface preparation and finishing. Specially mentioned are degreasing by condensation of chlorinated solvents, cleaning by using the metal as an anode in an acid electrolyte and the two types of wash primers.—RPI.   19574

5.9.4, 6.4.4

Anodic Protective Coating on Magnesium: The Cr-22 Process—A Depletion Study. R. Wick and M. Reed. Metal Finishing, **57**, No. 4, 68-70 (1959).

A Cr-22 bath (CrO_9-HF-H_3PO_4-NH_4OH) was operated over an extended period. Coating weight and thickness and corrosion-resistance decreased throughout the run, but could be restored by replenishment. This can be controlled on the basis of coating thickness and weight, or by relating amp.h or sq. footage of treated metal to bath composition.—MA.   19576

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.5, 3.7.2, 3.2.2

Stainless Steels to Combat Corrosion. G. E. Rowan. Paper before Can. Inst. Mining & Met. Hamilton, Ont., Feb. 23, 1958. Trans. Can. Inst. Mining and Met., **62**, 127-132 (1959); Can. Mining and Met. Bull., **52**, No. 564, 255-260 (1959) April.

Discussion of ability of stainless steel family of alloys to resist corrosion. Steels with a Cr content of 12 include Types 410, 403, 420, 416, 405 and 12-12 (12 Ni). 17 Cr alloys, with more resistance to corrosion than 12 Cr group include Types 430, 431, 440 and 301 (7 Ni). Most important group of austenitic alloys is 18 Cr, 8 Ni group including Types 302, 304, 305 and 308; problem of carbide precipitation in these alloys is discussed. High-Cr alloys Type 442 (20 min. Cr) and Type 446 (23-27 Cr) were developed to overcome corrosion or oxidation problems. Development of Cr-Ni alloys of modified analyses for special applications is considered; examples include Type 316 (2-3 Mo), Type 317 (3-4 Mo), Type 303 (additions of Se, P or S), etc. Hazards to successful use of stainless steel are intergranular, galvanic, contact, pitting or pinhole, and

stress corrosion. Preventive measures are discussed. Elimination of corrosion failure by suitable changes in design and fabrication is considered. Principal stainless alloys used by various Canadian industries are tabulated. Graphs show effect of additions of Cr to iron on corrosion rate in industrial atmospheres, and expansion rates for stainless steels compared with other metals and building materials. Photomicrographs illustrate carbide precipitation in Type 302 and transgranular stress corrosion cracking in Type 304.—INCO.   19439

6.2.1
The Investigation of Corrosion Failures of Ferrous Metals. E. E. White and K. A. Chandler. Paper before Corrosion Group, Soc. Chem. Industry, March 4, 1959. Chemistry and Industry, No. 33, 1028-1035 (1959) Aug. 15.

Three aspects to any investigation of corrosion failures are: history or background of problem, inspection of failure (assessment of corrosion damage, assessment of protective measures, corrosive environment, design features), and laboratory and field tests. A number of practical cases are discussed, subdivided by environment of exposure as follows: air (steel roof supports, steel balustrading, telephone insulator in service in Fiji, steel sheets of Nissen huts); fresh waters (economizer tubes, boiler condensate lines, domestic water supply lines); soils (gas pipelines, steel guy ropes); concrete (steel embedded in damp concrete); marine and river water (steel pontoons); miscellaneous (corrosion of stainless steel in gelatine solutions containing SO_2, stainless steel jug used to hold soup, water cistern made from enameled steel, mild steel scrolls used in a machine for conveying fish pulp). In most cases failure is due to one or more of following reasons: incorrect choice of preventive measures, poor application of preventive measures, inadequate maintenance, incorrect choice of steel, inadequate surface preparation of steel, poor design features, or inadequate treatment of corrosive medium. Photos, graphs, 5 references.—INCO.
19583

6.3 Non-Ferrous Metals and Alloys—Heavy

6.3.20, 3.6.8, 3.8.3
Hydrogen Discharge Overvoltage at Zirconium in Acid and Alkaline Solutions. (In Russian.) A. M. Murtazaev and T. K. Azizova. Uzbek. Khim. Zhur., Akad Nauk Uzbek. S.S.R. (Uzbekistan Chem. J., Akad. Sci. Uzbekistan SSR), No. 3, 69-74 (1958). U. S. Atomic Energy Commission Translation No. 3728 on Deposit at the Special Libraries Assoc. Translation Center. Photocopies Available from John Crerar Library, 86 E. Randolph St., Chicago 1, Illinois, ATTN: Special Libraries Translation Center. Also from: Library of Congress, Photoduplication Service, Washington 25, D. C.
Hydrogen overvoltage of zirconium was measured at current densities ranging from 10^{-5} to 10^{-1} amp/cm^2 in neutral, acidic and basic solutions. Zirconium is readily passivated in alkaline solutions. It was shown that when the acid concentration is increased by a factor of 10, the hydrogen overvoltage of zirconium is diminished by approximately 60 millivolts, and by 75 millivolts in the case of the alkali.—NSA.   18876

6.3.5, 3.7.2
Preliminary Study of the Effect of Binary Alloy Additions on the Oxidation Resistance of Columbium. F. J. Clauss and C. A. Barrett. Lewis Flight Propulsion Lab. Paper before Electrochem. Soc., Symposium on Columbium, Washington, May 15-16, 1958, pp. 92-97 of book, "Technology of Columbium," Edited by B. W. Gonser and E. M. Sherwood, John Wiley & Sons, New York, 1958.
Investigation conducted as qualitative screening to indicate binary alloys of niobium that might warrant further study. Addition elements reported herein are: nickel, titanium, vanadium, chromium, zirconium, molybdenum, tantalum, tungsten, iron, cobalt, iridium, aluminum, silicon, copper, germanium, selenium and rhenium. They were added singly to niobium in 1, 2, 5, 10 and 25

at.% and specimens were fabricated by powder metallurgy. Nature of scale and resistance to oxidation of these binary alloys were evaluated by continuous exposure to dried air for 4 hrs. at 1000 C and 2 hr. at 1200 C. Iron, cobalt and nickel form low-melting eutectics with niobium, and this caused specimens containing higher concentrations of these 3 elements to fuse during sintering at 3100 F. The 5-at.% iron and 5-at.% cobalt specimens had lower oxidation rates than pure niobium at 1000 and 1200 C. 25 at.% iridium also gave low rate. Nickel gave little or no improvement. Graphs.—INCO.   18853

6.3.20, 4.3.2, 1.2.5
Reactions of Zirconium and Zirconium Based Alloys with Nitric and Nitric-Hydrofluoric Acids. Part I. Hazardous Aspects. Part II. Dissolution Rates. F. S. Martin and B. O. Field. United Kingdom Atomic Energy Authority, AERE-C/R-2692, December, 1958, 16 pp. Available from United Kingdom Atomic Energy Authority, Research Group, Atomic Energy Research Establishment, Harwell, Berks, England.
Hazardous aspects of the dissolution of zirconium-uranium alloys in nitric acid were studied. It is concluded that when nitric acid constitutes the major part of the dissolving solution (i.e., if fluoride concentrations are low), the safe dissolving of such alloys cannot be guaranteed. The explosive reactions observed are not of the detonation type, but appear to involve a rapid oxidative reaction between adsorbed or precipitated nitrates and finely divided metal (or metal in a low oxidation state) on the alloy surfaces. Some dissolution rates are reported for 5% uranium-Zircaloy-2 and for Zircaloy-2 in nitric acid-fluoride mixtures, in sulfuric acid catalyzed by ferric ion, and in anhydrous dinitrogen tetroxide in tributyl phosphate. (auth)—NSA.   18869

6.3.8, 4.3.3, 4.3.2, 3.7.2
Corrosion Resistance of Lead and Lead Alloys. Pt. II. Lead, Lead-Antimony, and Lead-Tin Alloys. (In Japanese.) Fumio Hirama and Noboru Watanabe. J. Japan Inst. Metals, **22**, No. 7, 345-347 (1958).
Lead and lead-antimony alloys were resistant to ammonium hydroxide, sodium hydroxide toilet-soap and magnesium chloride-sodium chloride solution, and lead-tin alloys to sulfuric acid and sulfuric acid-ammonium sulfate solution. In sulfuric acid plus nitric acid, lead-tin alloys were less resistant than lead and lead-tin alloys.—MA.
For Pt. I. See Card No. 16501 Classified 6.3.8, .4.3.2, .3.7.2   18728

6.3.19, 3.7.3
Effect of the Nature of the Heating Atmosphere on the Oxidation of Zinc Powder. (In German.) G. Ogiermann and H. Weik. Metalloberfläche, **12**, No. 7, 199-201 (1958).
When zinc powders of various particle-size are heated for up to 24 hrs. at 150-400 C, oxidation (as shown by increase in wt) is much greater in air than in an atmosphere of commercial nitrogen (containing 2.5% oxygen), and greater with fine-grained powders, owing to their greater specific surface, than coarse-grained powders.—MA.   18918

6.3.6, 2.2.7, 2.3.8, 3.2.2
Design of Test Systems for Studying the Corrosion of Copper and Copper Alloys by Various Types of Water. M.

F. Obrecht and L. L. Quill. Paper before Engrs.' Soc. West. Penna., 19th Ann. Water Conf., Pittsburgh, Dec. 8, 1958. Proc. 19th Ann. Water Conf., Engrs' Soc. West Penna., **1958**, 33-51; disc., 51-63.

Report of research jointly sponsored by Copper and Brass Research Association and Michigan State University. Experiences with copper and copper alloy distribution systems at Michigan State University are detailed. Service failures, field test and test panel design, operation and some test results are recorded. Typical examples of failures are shown. Both erosion and corrosion played a part in pitting. Examples of localized pitting believed to be concentration cell attack were also found. Test locations were carefully chosen for installation of NDHA-ASTM copper cor-

rosion test specimens and strip testers. Test loops were installed at key locations. Relatively simple pilot plant for studying effects of temperature, water velocities and types of waters on copper and copper alloy tubing was designed. Equipment can be modified easily to include additional temperatures or water velocities as part of a single experiment. Materials included copper and red brass. Measurements of amount of corrosion were determined by micrometric, radiographic methods and loss of metal by weight. Number and severity of failures in University water distribution system has been decreased by controlling flow rates, reducing oxygen and carbon dioxide concentrations, by improving and controlling regeneration in water softening and by maintaining positive Langelier index by blanding and chemical ad-

ditions. Studies are continuing with other alloys and different types of water. Photos, photomicrographs, tables, graphs.—INCO.   18901

6.4 Non-Ferrous Metals and Alloys—Light

6.4.2
Corrosion Resistance of Aluminum and Aluminum Alloys. F. C. Porter. Corrosion Prevention and Control, **6**, No. 5, 36-44 (1959) May.

Comprehensive review covers: formation of protective oxide film; types of corrosion encountered (pitting, intercrystalline, filiform, stress and layer corrosion); resistance to various atmospheres; chemical resistance (sea and tap water, inorganic salt solutions, acids, alkalies and organic compounds); effects of physical factors (temperature and velocity) on corrosion; contact with other materials (concretes, cement, plaster, brickwork, stonework, timber, plastics and paper) and with other metals (bi-metallic effects); mechanical and design factors; methods of protection (cathodic protection, anodizing, chemical conversion coatings, painting, vitreous enameling and plating including Kanigen Ni); and aluminum as coating metal (sprayed coating, hot dip aluminizing, plating and vacuum deposition). Table listing chief British Standard wrought and cast aluminum alloys (B.S. 1470-77, 1490) gives nominal composition, atmospheric corrosion resistance and finishing evaluation. 17 references.—INCO. 18487

6.4.3
Mechanical and Technological Properties of Beryllium. (In German.) Hans-Richard Meininghaus. Atomkernenergie, **4**, 231-232 (1959) June.

A brief outline of the mechanical strength and stretch properties is presented. Some details of the powder metallurgy, rolling and extruding of the metal is provided. Problems arising from welding and soldering are described. The corrosion resistance properties of beryllium are briefly mentioned. (auth)—NSA.   18430

6.4.2, 5.9.4
Anodic Oxidation of Aluminium Alloys Containing Silicon. (In French.) H. Richaud. Paper presented at the Fall Meeting of the French Metallurgical Soc., Paris, France, October, 1958. Mém. sci. Rev. Met., **56**, No. 1, 30-34 (1959).

The grey color obtained by anodic oxidation of Al-Si is not affected by the Si content in the range 1-5 percent. Increasing thickness of the oxide layer causes the color to darken, and it becomes lighter as the degree of cold working increases. Uniformity of color is achieved by treating homogenized material and for this reason all components of any assembly should be similarly treated.—MA.   19436

6.4.3, 3.7.4, 3.8.4
Structure and Growth of Beryllium Oxide on Single Crystals of Beryllium. (In English.) V. D. Scott. Acta Crystallographica (Denmark), **12**, No. 2, 136-142 (1959).

Electron diffraction and electron microscopy were used to study beryllium oxide films formed by heating single crystals of beryllium in air. The oxidation rate increased with temperature and the amount of randomly oriented beryllium oxide increased until only random growth occurred at 600 C. Between 300

and 400 C epitaxial growth on beryllium (001) cleavage was found. At approximately 800 C a (001) habit of the random beryllium oxide crystals developed. The diameter of the oxide crystals was approximately 10 A below 300 C and approximately 1000 A at approximately 800 C. The beryllium oxide layer gives little protection to the beryllium substrate above 600 C. The oxide grows out in needles up to 5 μ long and several hundred A thick; thin flakes of beryllium oxide also form at this temperature. 37 references.—MA.   18679

6.4.2, 4.4.5, 3.8.2
Reaction of Aluminum and Carbon Tetrachloride. Pt. II. R. H. Brown, E. H. Cook, M. H. Brown and J. D. Minford. J. Electrochem. Soc., **106**, No. 3, 192-199 (1959) March.

Mechanism of the reaction between aluminum and boiling carbon tetrachloride appears to be electrochemical. Conductivity measurements indicate that the reaction starts as soon as the aluminum is exposed to the boiling solution. The increase in the conductivity with time is caused by the presence of aluminum chloride and parallels the increase in weight of aluminum reacted as the reaction proceeds. The application of a cathodic current prevents attack of an aluminum specimen, indicating that the initial attack is caused by the presence of an ionic species. Trace amounts of the reaction product hexachloroethane were produced electrochemically in the absence of any aluminum.

Substances that retard the reaction apparently function by forming inactive complexes with the aluminum chloride. The rate-determining step in the reaction does not appear to involve free radicals since the majority of the effective inhibitors failed to react with known free radicals. 7 references.   17697

6.4.2, 2.2.7, 4.6.1, 3.6.6
Corrosion of Sheet Aluminium by Rainwater Containing Copper and Zinc Salts. (In Italian.) G. Luft. Alluminio, **28**, No. 3, 115-120 (1959) Mar.

To determine the corrosion-behavior of super-purity aluminum, commercial purity aluminum and Aluman alloy subjected to the effects of rainwater containing salts of heavy metals, various types of a composite setup, each comprising two samples of dissimilar metals, were installed at the Novara corrosion testing grounds. The arrangement of the metal samples was such as to permit rainwater to wet first the one and then the other, while care has been taken to avoid galvanic contact between the samples. The detailed results of the tests are tabulated. From these it appears that both the unalloyed aluminum, regardless of its purity, and the Aluman alloy, whenever they were coupled with copper being in the upper position, have suffered heavy galvanic corrosion damage of the pitting type. Zinc salts, on the other hand, did not cause appreciable surface deterioration on aluminum. Duration of the test was five years.—ALL.   18421

6.4.2, 4.6.1, 8.4.5
Corrosion Behavior of Aluminum-Nickel-Iron Alloys in High Temperature Water Under Dynamic Conditions. G. J. Biefer and P. G. Anderson. Atomic Energy of Canada, Ltd., CRMet-799, December, 1958, 65 pp. Available from Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

In dynamic corrosion tests in deion-

ized water at 260 C and 20 fps linear velocity, corrosion rates of approximately 8 x 10⁻⁴ in./yr. are obtained for aluminum-nickel alloys by using beds containing high areas of aluminum-nickel to saturate the loop water with dissolved corrosion product. Preliminary tests indicate that further reductions in corrosion rate are obtained by giving the test specimens a pretreatment in high tem-

perature static water. Replacement test specimens are observed to corrode more rapidly than original specimens. Possible mechanisms for these effects are discussed. (auth)—NSA.   18726

6.4.2, 3.7.2, 4.6.1, 8.4.5
Effects of Alloying Additions and Temperature on the Corrosion of Aluminum-Nickel-Iron Alloys in High Tem-

perature Water. G. J. Biefer. Atomic Energy of Canada, Ltd., CRMet-796, July, 1958, 50 pp. Available from Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

Corrosion resistance of a number of aluminum-nickel-iron alloys has been studied in static water at 260 to 350 C. Small additions of titanium, zirconium and beryllium were found to improve the corrosion resistance. The effect of increased nickel (demonstrated previously) and these minor additions was found to be additive, and the alloy of best corrosion resistance (AECL-10197) had the wt.% composition: nickel, 2.0; iron, 0.5; silicon, 0.2; titanium, 0.2; zirconium, 0.05; and beryllium, 0.05. At 300 C, the static corrosion rate of 10197 was 0.5×10^{-3} inches/year. The significance of the results is discussed in terms of reactor technology and the mechanism of corrosion. (auth)—NSA.   18725

6.4.2, 6.6.5, 3.7.2
On the Corrosion of Aluminum and Its Alloys by Cement Mortar and Its Prevention. (In Japanese.) G. Ito. Report of Scientific Research Inst. (Rikagaku Kenkyusho Hokoku), **34**, No. 1, 76-79 (1958) Jan.

Corrosion of aluminum and its alloys in contact with cement mortar is caused by calcium hydroxide. The corrosion rate of 99.99% aluminum is the same as in sea water, i.e. approximately 0.0023 mg/cm^2/hr at 40 C. Alloying with magnesium or silicon prevents corrosion; 5% magnesium is required.

Corrosiveness of cement can be inhibited by addition of silica rich material.—JSPS.   18799

6.4.2, 8.4.5, 3.5.9, 4.6.1
Irradiation of Aluminum—Plutonium Alloys in Zircaloy Sheathing. Pt. I. Preliminary Experiments with Aluminum-Uranium Alloys. T. I. Jones. Dec., 1958, 24 pp. Atomic Energy of Canada Ltd., Chalk River, Ontario, Canada. (AECL-735; CRFD-810).

Aluminum-uranium alloys containing up to 20 wt.% uranium were studied in a stand-in capacity as a prelude to a program of work with aluminum-plutonium alloys clad in Zircaloy-2. The object of the investigation was to examine the effect of temperature on the structure and hardness of the core alloys, their interaction with Zircaloy-2 at various temperatures, and their corrosion properties in high-temperature water. Diffusion bonds were formed between Zircaloy-2 and aluminum-10 wt.% uranium alloy by heating at 600 C for one hr. However, the large difference in expansion co-efficients caused failure of the bonds during cooling. Heating at immediately above the solidus temperature (640 C) of the core alloys caused rapid sheath dissolution, sheath integrity being maintained for only a few hours. Hypo-eutectic alloys possessed good resistance to water at 340 C (0.004″ penetration in 2 hrs) whereas exfoliation 0.040 to 0.080″ deep occurred with the hyper-eutectic alloys. Aluminum-10 wt.% uranium alloys, canned with defected Zircaloy-2 sheathing, was as resistant to corrosion in water at 340 C as the corresponding bare alloy. (auth)—NSA.   18807

6.4.2, 3.7.2, 2.3.9
Electron-Diffraction Study of the Oxidation of Aluminum Alloys. (In Russian.) Iu. D. Chistiakov and M. V. Mal'tsev. Kristallografiya (Crystallography), **2**, No. 5, 620-625 (1958). English Translation of Journal Available from Am. Inst. Physics, 335 E. 45th St., New York 17, N. Y.

Effect of additions of beryllium, lithium, cadmium, strontium, barium and magnesium on oxidation of aluminum alloys. 10 references.—RML.   18855

6.6 Non-Metallic Materials

6.6.6, 3.8.4
Stability of Ceramics in Hydrogen Between 4000 and 4500 F. Charles E. May, Donald Koneval and George C. Fryburg. National Aeronautics and Space Administration Memo 3-5-59E, March, 1959, 13 pp. Available from National Aeronautics and Space Administration, Lewis Research Center, Cleveland.

Extent of reaction of hydrogen with various carbides, nitrides, borides and oxides was studied in a static system. Most of these materials, hafnium carbide, zirconium carbide, titanium carbide, tantalum carbide, niobium carbide, tungsten carbide, molybdenum dicarbide, hafnium nitride, zirconium nitride, niobium nitride, zirconium diboride, niobium diboride and tungsten boride, showed less reaction than the minimum detectable value. However, the data seem to indicate that the ceramics, titanium nitride, tantalum nitride, hafnium diboride, titanium diboride, zirconium dioxide and chromic oxide had reacted. Reactions of silicon carbide, vanadium carbide and tantalum diboride were not determinable because of their incompatibility with the tungsten container. (auth)—NSA.   18441

6.6.6, 4.3.2, 4.3.3
Corrosion Resistance of Borides of Columbium, Tantalum and Tungsten. (In Ukrainian.) K. D. Modylevskaya and G. V. Samsonova. Ukrain. Khim. Zhur., Akademii Nauk Ukrain. (Ukrainian Chem. J.), **25**, 55-61 (1959) Jan.

Borides of niobium tantalum and tungsten have a high resistance to acid and caustic soda corrosion at room temperature. 6 references.—RML.   18446

6.6.6, 3.5.9, 3.8.4
Oxidation of Hot-Pressed Titanium Carbide and Titanium Boride in the Temperature Range 300-1000 C. N. F. MacDonald and C. E. Ransley. Powder Met., No. 3, 172-180 (1959).

Oxidation characteristics of pure hot-pressed titanium carbide and titanium diboride were studied in the range 300-1000 C. Titanium carbide shows a very marked peak in the rate of oxidation at approximately 450 C, the oxidation product at this temperature being anatase (TiO_2), which is powdery and non-adherent; the oxidation follows a linear law.—BTR.   18402

6.6.8, 7.2, 5.4.5
Plastic in Distribution Piping. H. M. McDaniel. Paper before Florida-Georgia Gas Assoc., 1958. Gas Age, **123**, No. 3, 25-28 (1959) Feb. 5.

Review of plastic and its advantages and disadvantages in piping for gas transport, with special emphasis on plastic coated steel pipe. History of its use is considered, along with problems encountered by Republic while developing its new plastic coated steel pipe, X-Tru-Coat. Since corrosion resistance is major advantage offered by plastic pipe and steel is the most economical pressure carrying material available today, these advantages are combined in new plastic coated steel pipe. Tests used to evaluate polyethylene coating included salt-crock test to determine ability of coating to prevent underfilm migration, salt spray and water immersion tests, thermal shock test and standard soil stress box. Photos show damaged areas on pipe samples tested as anode and as cathode in salt-crock test.—INCO.   18413

8. INDUSTRIES

8.3 Group 3

8.3.4, 5.3.4
Protective Coatings Against Corrosion in Breweries. R. Bunger. Brauwelt, No. 30, 537-540 (1958); Metal Finishing Absts., **1**, No. 3, 109 (1959).

Corrosion in breweries is accelerated by heat, inorganic and organic acids,

alkalies, cleansers, salts and water. Protective air drying, stoving and catalyzed finishes are reviewed.—RPI.   18848

8.3.4, 3.8.2, 3.6.2, 3.4.9

Practical Solutions to Corrosion in the Brewing Industry. D. H. Edmonds. J. Inst. Brewing, 65, 398-405 (1959) Sept.-Oct.

Nature of corrosion, electrochemical theory and factors controlling corrosion rate-humidity, atmospheric pollution and concentration cells.—RML.   19108

8.3.5, 7.5.2, 6.3.14, 3.2.2, 2.3.9

Electron Metallographic Evidence of Diffusion of Hydrogen Through Tin Plate Containers. Elma Lanterman. J. Applied Phys., 30, 1084-1086 (1959) July.

Rupture and blistering of the exterior tin surface of containers which had failed prematurely due to excessive hydrogen formation by corrosion processes within the container when packed with grapefruit juice.—RML.   18382

8.4 Group 4

8.4.5, 3.4.3

Corrosion Product Activity in the Primary System of the Army Package Power Reactor. Alco Products, Inc. U. S. Atomic Energy Commission Pubn., APAE-29, April 15, 1958, 73 pp. Available from Office of Technical Services, Washington, D. C.

Experimental work has been performed to determine the extent and mechanism of the buildup of activated corrosion products in the primary system of the Army Package Power Reactor. The results of radiochemical analyses of water and crud sampled from the primary system, and of deposits removed from the surface of metal test specimens exposed to the primary coolant are presented. In addition, the dose rates measured during reactor shutdown at the external surfaces of primary system components are reported. Water, crud, and deposits from the metal test samples were analyzed for long-lived gamma emitting nuclides only. Data are presented on the specific activity of these samples and the nuclide ratios of these specific activities. The buildup of activity on the surface of the metal specimens is shown to be related to time of exposure, temperature of the coolant, and the type of steel specimen used. (auth.)—NSA.   18691

8.4.5, 7.2, 3.6.2, 5.7.7

How to Avoid Piping Corrosion in Nuclear Reactor Plants. W. Z. Friend. Heating, Piping and Air Conditioning, 30, No. 12, 105-108 (1958) Dec.

Consideration of characteristics of piping materials, operating temperature of system and chemical composition of liquid to be piped; principal primary parts; discussion of crevice and stress corrosion; control of pH of great importance in ability of steel to resist corrosion; corrosion resistance of various metals; addition of dissolved hydrogen gas most effective in suppressing dissociation of water and reducing corrosion. —BL.   18757

8.4.5

Corrosion in the Atomic-Energy Industry. M. D. Jepson, D. White and B. L. Harbourne. Proc. Corrosion Convention (London), 1957, 1958, 35-39; disc., 39-40.

Corrosion problems encountered in power reactors are discussed, also those connected with steam-rising plant and

a few examples of a general nature, e.g., avoidance of carrying scale into the reactor and the protection of equipment requiring repeated decontamination.— MA.   18806

8.4.5, 6.3.3

Analysis of the Status of Chromium in Solution Under In-Pile Conditions. J. C. Banter, J. E. Baker and R. J. Davis. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-58-7-63, July 15, 1958, 27 pp. Available from Office of Technical Services, Washington, D. C.

A summary of the chromium data from the HRP in-pile corrosion program is examined in an effort to determine the chromium species present in such solutions under in-pile conditions. Data from previous in-pile bomb and loop experiments pertinent to chromium behavior are tabulated and correlations are offered to support a proposed model. It is pointed out that other interpretations of the same data are possible, and to obtain conclusive evidence as to the identity of chromium species in these solutions, especially designed experiments are necessary.—NSA.   18699

8.4.5, 7.4.1, 3.4.3, 5.7.2

Investigations of the Contaminants in the First Nuclear Power Plant Water Cooling Circuit. (In Russian.) P. N. Slyusarev, V. A. Ivanov and L. N. Nesterova. Atomnaya Energiia (Atomic Energy), 6, 639-643 (1959) June. English Translation of Journal Available from Consultants Bureau, Inc., 227 West 17th Street, New York 22, N. Y.

Rate of primary water contamination by 1X18H9T steel corrosion was investigated. It was found that the corrosion

rate is proportional to the purge rate and to reactor power. Using radiochemical, analytical, electrodialysis and ultra-filtration methods, it was shown that cobalt, chromium, manganese, sodium and nickel were present as ions while copper and iron appeared in a colloidal state. The use of deaerated water and change in surge tank design were recommended. —NSA.   18595

8.4.5, 6.3.21, 3.5.4

A Study of Some Mechanical, Physical and Corrosion Properties of Iodide Hafnium. J. G. Goodwin and F. R. Lorenz. Westinghouse Electric Corp. Nuclear Sci. and Eng., 6, No. 1, 49-56 (1959) July.

Five 30-lb, 4-in.-diam. iodide hafnium ingots representing material typical of that utilized for the Shippingport Pressurized Water Reactor were fabricated into strip. Typical tensile, impact, hardness, corrosion test weight gain, electrical resistivity and chemical analysis values were obtained by testing samples from each strip. The effect of irradiation on the impact strength and hardness of hafnium strip was investigated by subjecting a total of 36 subsized Izod impact specimens to irradiation for two cycles in the Materials Testing Reactor. A duplicate group of nonirradiated specimens was used as a control group. The mechanical, physical and corrosion property measurements for the nonirradiated and irradiated samples showed no physically significant differences attributable to chemical analysis. The impact strength and hardness values for the irradiated specimens showed differences which were attributable to the integrated neutron flux received. (auth.)—NSA. 18365

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Topic of the Month

Chloride Stress Corrosion Cracking Of Stainless Steel Deaerator Trays*

By N. D. GROVES*, L. R. SCHARFSTEIN* and C. M. EISENBROWN*

Introduction

AFTER SEVERAL months' service, deaerator trays fabricated from AISI Type 201 and Type 329 (Carpenter 7 Mo) stainless steels were reported to have failed by chloride stress corrosion cracking. The trays were used in a 300,000 lb per hr deaerating feed water heater. The deaerating heater is a large Inconel and Type 304 stainless steel lined vessel containing stacks of trays down through and over which the feed water flows to be stripped of oxygen by steam entering at the bottom.

The feed water at 62 F, containing 10 ppm chloride, 48-51 ppm dissolved solids, hardness 13 ppm (as calcium carbonate) and pH of 7.1-7.3, entered a distributing box at the top of the heater.

The water then enters the stacks of trays from V-notch weirs and flows down through the unit to be heated by steam entering at the bottom. The unit is normally maintained at 5 psi and 227 F.

The deaerator trays have been fabricated primarily from AISI Type 304 stainless steel. This material worked satisfactorily, except in the first and second layer of deaerator trays at the top of the heater. Scale build-up and concentration of chlorides have occurred at the ends of these trays in the upper level. This has resulted in severe cracking at the ends of some of the trays.

Scale build-up and concentration of chlorides are restricted to the ends of the upper two layers of trays (directly under the distributing box) because they are alternately wet and dry. The trays in

Abstract

A case history is given of failures of stainless steel deaerator trays used in a deaerating feed water heater. Trays fabricated from Type 201 and Type 329 stainless steels were reported to have failed by chloride stress corrosion cracking after several months' service. The cracking of the Type 201 was very severe. It is shown that conditions in parts of the deaerating heater promote failure by chloride stress corrosion cracking and the service life of austenitic stainless steels is very short. Annealing after welding of the Type 329 trays would improve resistance to cracking. It is also suggested that Type 430 stainless steel be considered since it is not susceptible to chloride stress corrosion cracking.   6.2.5, 3.5.8, 7.6.8

the lower layers are wet continuously because of complete water distribution over their entire surfaces. The oxygen concentration is also highest in the upper part of the heater. Materials of construction for deaerator trays in the upper two layers have included AISI Types 304, 329 and 201 stainless steels and Inconel.

Discussion

Two failed deaerator trays are shown in Figures 1 and 2. Chemical analyses verified that Tray A was fabricated from AISI Type 201 stainless steel and Tray B from Type 329. It is evident from Figures 1 and 2 that the tray fabricated from AISI Type 201 stainless steel was

TABLE 1—Chemical Analysis of Tray Steels

Identification	ELEMENT				
	C	Mn	Cr	Ni	Mo
Tray A (Type 201)	.09	7.22	18.18	5.25	.18
Tray B (Type 329)	.08	....	27.37	4.21	1.68
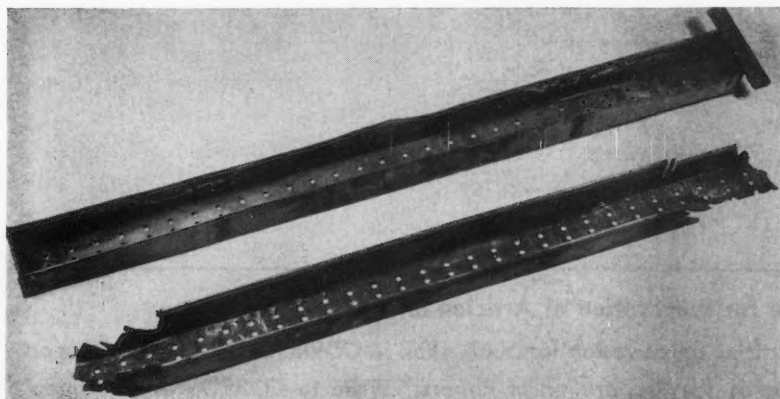
Figure 1—Photograph of failed deaerator trays Tray A (bottom) was fabricated from AISI Type 201; Tray B (top) fabricated from AISI Type 329. Approximately 1/10 X.
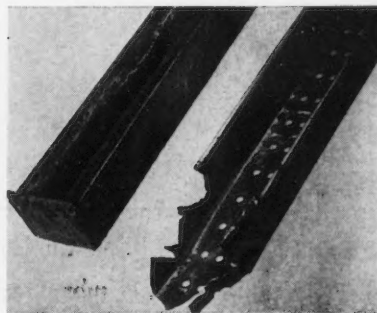
Figure 2—Photograph showing attack at ends of deaerator trays. Tray A (right) was fabricated from AISI Type 201; Tray B (left) was fabricated from AISI Type 329. Approximately 1/8 X.

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Figure 3—Crack adjacent to weld at end of Type 329 tray (Tray B). Approximately ¼ X.
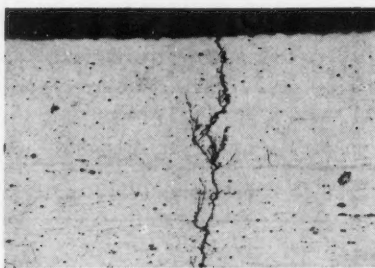
Figure 4—Section through crack in Type 201 deaerator tray. Approximately 125X; etchant was picric and hydrochloric acids.
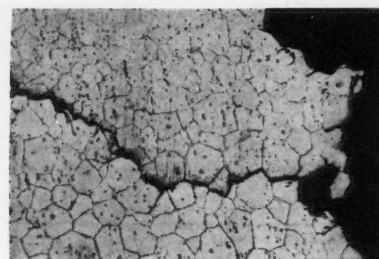
Figure 5—Section through crack in Type 329 deaerator tray. Approximately 50 X; etchant was ethyl alcohol and hydrochloric acid.

severely cracked at both ends, while the tray fabricated from Type 329 was completely intact showing only one crack at one end near the weld (Figure 3). Micros from the cracked area of each tray are shown in Figures 4 and 5. The cracks in the Type 201 (Figure 4) are typical transgranular stress corrosion cracks. The crack adjacent to the weld in the Type 329 (Figure 5) is predominantly intergranular following the austenite and second phase in the boundaries. It is difficult to conclude whether the crack is indicative of stress cracking or stress corrosion cracking; however, welding

stresses and the grain boundary precipitate caused by the welding operation, which was not followed by annealing, would cause the material to be susceptible to cracking by either mechanism.

Conclusion

Conditions in the deaerating heater, particularly in the upper section, promote failure by stress corrosion cracking. Austenitic stainless steels in this region fail rather severely in several months by chloride stress corrosion. Type 329 has demonstrated much better resistance to failure by cracking than the austenitic

stainless steels in this particular environment.

Annealing, following welding of the ends of the Type 329 trays, should greatly reduce susceptibility to cracking by minimizing intergranular precipitation and stresses. It is also suggested that a ferritic stainless steel, such as AISI Type 430, be used as a material of construction for deaerating trays in the upper portion of the heater. It is believed that this stainless steel would exhibit satisfactory general corrosion resistance and, in addition, the ferritic stainless steels are not susceptible to chloride stress corrosion cracking.

Any discussion of this article not published above will appear in June, 1961 issue.

Influence of Reactor Radiation on the Oxidation of Niobium*

By J. V. CATHCART and F. W. YOUNG, JR.

Introduction

A STUDY of the influence of reactor radiation on the oxidation characteristics of niobium was undertaken in order to investigate the effect of such radiation on oxidation mechanisms. Under conditions for which the ionization of the oxidizing gas is not the rate-determining step, two important ways in which neutron irradiation might be expected to influence the gaseous oxidation of metals are (1) through a change in the total number of lattice defects in the oxide film, and (2) by the alteration of some nucleation step in the oxidation process. In instances where the oxide film formed on a metal is relatively thick and nonporous, the rate-determining step is usually the diffusion of lattice defects across the oxide film; thus, a significant increase in defect concentration should produce an increase in the rate of oxidation. With regard to the second effect, highly localized additions of energy to the oxide lattice might be expected to trigger certain types of nucleation steps and again produce an increase in the oxidation rate.

The practical significance of these possible radiation effects is obviously related to the neutron flux to which the specimens are subjected, and it is useful to consider in a qualitative way the extent of damage likely to be produced by currently readily available neutron fluxes (up to $\sim 10^{13}$ nv). An order-of-magnitude estimate of the changes to be expected in a typical oxidation process may be obtained in the following way. Assume that each neutron produces 10 defects/cc of oxide[1] and that each defect

★ Submitted for publication April 28, 1960.

Abstract

The effect of neutron irradiation at flux levels of $\sim 10^{12}$ nv on the oxidation characteristics of niobium was studied at temperatures near 400 C. No measurable change was detected either in the rate of oxidation of niobium or in the nucleation process associated with the oxidation of niobium. On the basis of estimates of the extent of radiation damage in thin oxide films, it was concluded that the damage resulting from irradiation at currently available neutron flux levels is unlikely to change the number of oxide lattice defects sufficiently to produce a significant change in the oxidation rate. It was thought though that alteration of a nucleation-type process was possible.   3.5.4, 6.3.5, 3.2.3

contributes to the oxidation process. Then for an oxide film 5000 Å thick and growing at a rate of 10 Å/hr and for a flux of 10^{12} nv, approximately 2×10^{11} defects $\cdot$ hr^{-1} $\cdot$ cm^{-2} could be formed in the film. However, the stipulated growth rate requires the addition to the film of $\sim 10^{15}$ cations and anions $\cdot$ hr^{-1} $\cdot$ cm^{-2} and, hence, the generation of $\sim 10^{15}$ defects $\cdot$ hr^{-1} $\cdot$ cm^{-2}. It is to be expected, therefore, that exposures to fluxes of the order of 10^{15}-10^{16} nv would be required before the oxidation rate could be changed appreciably as a result of a shift in defect concentration.

In a similar manner, a rough estimate of the number of regions of localized disorder introduced into the film by neutron bombardment may also be obtained. Assume that 10^{-1} such regions are created per cubic centimeter of oxide per unit of flux. Then a flux of 10^{12} nv would produce $\sim 2 \times 10^{10}$ regions of disorder per square centimeter of a 5000-Å film in one hour. The maximum density of various types of oxide nuclei generally ranges from 10^7 to 10^{10}/cm^2. (These calculations

Cathcart   Young

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have been based on 5000 Å films, since this approximate thickness is of especial interest in the oxidation of niobium.)

It was, therefore, concluded that extremely high neutron fluxes are probably necessary to produce a measurable effect on the oxidation rate of metals as a result of changing the defect concentration in the oxide film. On the other hand, a neutron flux of only 10^{12} nv could in one hour generate potential nucleation sites in the oxide in numbers at least of
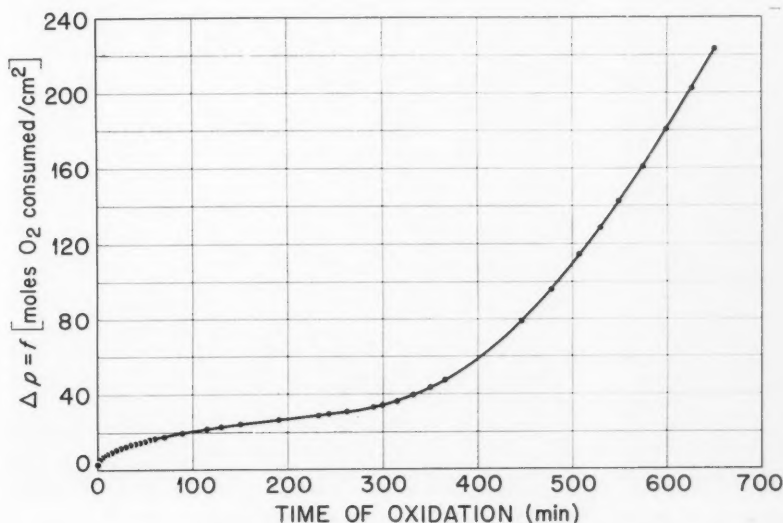
Figure 1—Oxidation rate curve for niobium at 400 C.
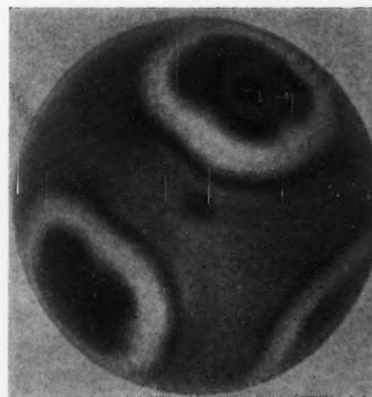
Figure 2—Single-crystal sphere of niobium oxidized for 24 hours at 350 C. Photograph illustrates the pattern of interference colors which develops on the crystal as a result of the variation of oxidation rate with crystallographic plane.

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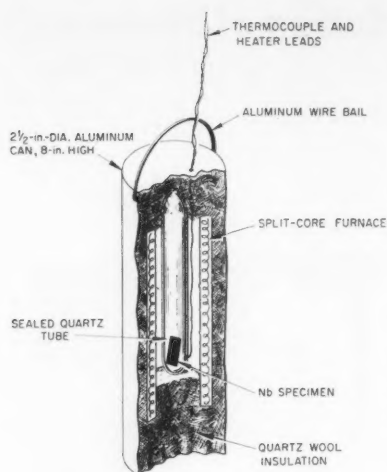
Figure 3—In-pile oxidation apparatus.

the same order of magnitude as the number of nuclei normally found in oxide films.

These ideas were tested through a study of the oxidation of niobium. Two features of the oxidation properties of this metal make it especially suited for these tests: (1) the oxidation process involves an easily studied nucleation step, (the formation of cracks in the oxide film) and (2) through the use of spherical single crystals, changes in the oxidation rate of niobium may be readily detected.

A typical oxidation rate curve for niobium in the vicinity of 400 C is shown in Figure 1. A function of the quantity of oxygen consumed per square centimeter is plotted against the time of oxidation. As indicated by the rate curve, niobium characteristically exhibits a transition from protective to nonprotective oxide formation in this temperature range. Previous work[2] has shown this

transition to be coincident with the formation of microscopic, blister-like cracks in the oxide film. In the absence of irradiation, the cracks generally begin to form when the film reaches a thickness of about 5000 Å, and the maximum number of such cracks generated is $\sim 10^7/cm^2$. The influence of neutron irradiation on the time required to initiate crack formation and on the number of cracks formed is easily measurable.

As with many other metals, niobium shows a marked variation of oxidation rate with crystallographic orientation; consequently, a pattern of interference colors develops on a single-crystal sphere of niobium as the sphere is oxidized (Figure 2). Differences in color in the pattern are, of course, related to differences in the thickness of the oxide film. Estimates thus may be made of the relative rates of oxidation of different crystallographic planes on the basis of these interference colors. Either an alteration in these relative rates or a uniform change in the oxidation rates over the crystal would lead to changes in the interference color pattern on the sphere. Thus through the use of monocrystalline as well as polycrystalline specimens, the in-pile oxidation of niobium could be evaluated in terms both of possible oxidation rate changes and changes in a nucleation process.

Experimental Procedures

The polycrystalline niobium specimens were in the form of coupons $1 \times 2 \times 0.03$ cm. Spherical niobium single crystals, $\frac{1}{2}$ inch in diameter, with cylindrical stems $\frac{1}{4}$ inch in diameter and 1 inch long were machined from large-grained, arc-cast niobium ingots. Prior to oxidation all samples were mechanically polished through 4/0 emery, lapped with Linde A alumina, and electropolished in a 10 per cent HF-90 percent H_2SO_4 bath. After a thorough wash with distilled water, the samples were placed in small quartz capsules and annealed overnight at 400 C at

a pressure of $\sim 10^{-6}$ mm Hg. They were then cooled to room temperature and the quartz capsules filled with sufficient purified O_2 to produce a pressure of one atmosphere at 400 C. Subsequently, the capsules were sealed off and placed in a small, split-core furnace contained in an aluminum can (see Figure 3). The entire assembly could easily be lowered into the ORNL graphite pile. Approximately 3 minutes were required to bring the furnace to 400 C inside the pile. The fast neutron flux to which the specimens were subjected during oxidation was $\sim 6 \times 10^{11}$ nv.

Niobium samples were oxidized at several temperatures between 380 and 450 C and for times ranging from 1 to 6 hr. At the completion of an experiment the samples were removed from the pile and the induced radioactivity allowed to decay for about one week. The samples were then subjected to both optical and electron microscopic examinations as previously described.[3]

Results

Electron microscopic studies of the polycrystalline niobium specimens showed that the reactor radiation failed to produce significant changes either in the time required for the initiation of blister formation in the oxide or in the number of blisters per square centimeter. Figure 4 is an electron micrograph of a niobium specimen oxidized 2 hr at 400 C in-pile. The corresponding result obtained in the absence of radiation is illustrated in Figure 5. In both cases the number of blisters observed was $\sim 10^7/cm^2$. The small differences in the background roughness in the two specimens were produced as a result of variations in the oxide surface topography as a function of crystallographic orientation and were not related to radiation effects.

Comparison of interference color patterns on single-crystal niobium spheres
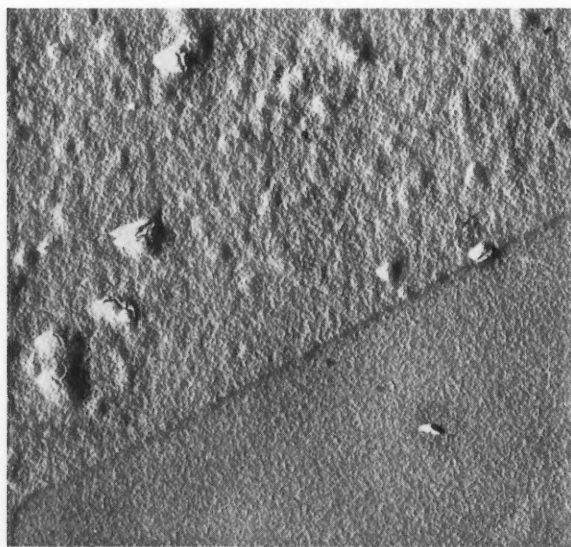
Figure 4—Electron micrograph of niobium specimen oxidized in-pile for two hours at 400 C. Carbon replica preshadowed with gold-manganin. Approximately 5400X.
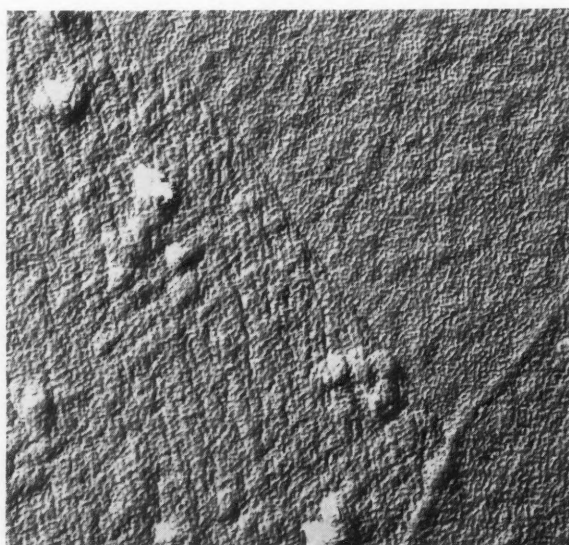
Figure 5—Electron micrograph of niobium specimen oxidized out-of-pile for two hours at 400 C. Carbon replica preshadowed with gold-manganin. Approximately 4600X.

likewise failed to indicate any significant influence of pile irradiation on the oxidation rate of niobium. For both out-of-pile and in-pile experiments, the areas near $< 100 >$ poles oxidized most slowly, while the oxidation rate was a maximum at $< 111 >$ and $< 110 >$ poles. Because of a lack of information regarding the index of refraction of the oxide, no absolute thickness values could be assigned to these oxide films. However, after 1 hr at 400 C, third-order interference colors were evident around the $< 111 >$ and $< 110 >$ poles, while the $< 100 >$ poles still exhibited first-order colors.

Discussion

The fact that neutron irradiation at a flux level of 6×10^{11} nv produced no significant changes in the oxidation rate of niobium is consistent with the previous conclusion that fluxes of $\sim 10^{15}$-10^{16} nv are required to change appreciably the defect concentration in an oxide film. This result is also in agreement with the observation by Young[3] that no change occurred in the oxidation rate of copper specimens on exposure to a neutron flux of $\sim 10^{12}$ nv. Yee,[4] on the other hand, on the basis of preliminary data, reported a significant increase in the oxidation rate of a zirconium specimen exposed to a fission-fragment flux of $5 \times 10^8/cm^2/sec$. The fast neutron flux required to produce an equivalent number of atomic displacements was estimated to be $\sim 10^{14}$-10^{15} nv. Thus the available evidence suggests that the production of oxide-film defects in concentrations large enough to alter oxidation rates measurably requires the use of either neutron flux levels generally unattainable at present or more efficient sources of radiation damage such as fission fragments.

The lack of any change in the time required for crack formation in niobium oxide films or in the number of such cracks likewise indicated that a neutron flux of $\sim 10^{12}$ nv does not influence crack formation in Nb_2O_5. Since the irradiation produced $\sim 10^{10}/cm^2$ regions of localized disorder in the film (i.e., $\sim 10^{10}/cm^2$ potential nucleation sites), it was concluded that the nucleation-type process associated with the oxidation of niobium was not affected by neutron irradiation. Presumably the energy required to initiate crack formation in Nb_2O_5 films is much larger than that to be associated with the regions of localized disorder produced by neutron bombardment. Further experimental work will, however, be required before the general applicability of these conclusions to other metal/oxygen systems can be precisely defined.

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Any discussion of this article not published above will appear in June, 1961 issue.

Corrosion Effects of Liquid Fluorine and Liquid Oxygen On Materials of Construction*

By F. W. FINK and EARL L. WHITE

Corrosion by Liquid Fluorine

Metallic Materials

FLUORINE is a liquid at atmospheric pressure over a relatively short temperature range. It has a freezing point of —363 F and a boiling point of —306 F. Liquid nitrogen, with a slightly lower boiling point (—320 F), is a convenient inert cooling liquid. Jacketed vessels, with liquid nitrogen in the annular space are used to keep liquid fluorine at or near atmospheric pressure and at about —310 F.

Although fluorine is the most chemically active of all elements, almost all of the common metals can be considered for its storage and handling. Two factors may be responsible for the low rates of attack of fluorine on the common metals. First, chemical reactions in general tend to proceed slowly at the low temperatures at which fluorine is a liquid. Secondly, protective films of fluoride compounds tend to form on metal surfaces and act as a barrier to further reaction. The extent of the protection provided by the fluoride films on metal surfaces is dependent upon the adherence and permeability of the coating.

A number of factors may decrease the effectiveness of these coatings. The formation of volatile fluoride compounds in the coatings may result in the breakdown of the protective films at temperatures above that of liquid fluorine. However, in liquid fluorine this is not so much of a problem, because even the more volatile fluorides (Table 1), such as those of carbon, boron, phosphorous, silicon, and arsenic are solids at —310 F. For fluorides that are volatile at room temperature, their presence in a surface film may promote film breakdown if the vessel is allowed to heat up.

The controlling factor in the corrosion behavior of metals in liquid fluorine is the solubility of the various metal fluorides that form in the coating in fluorine. Numerical solubility data for fluorine compounds have not been found in the literature. However, service data indicate that the fluorides of nickel, copper, chromium, iron, and probably many other metals are quite insoluble in liquid fluorine. It is believed that, as a protective film builds up and the rate of reaction slows down, an equilibrium between reaction rate and solubility of the film will be reached and a relatively steady corrosion rate will prevail. Unfortunately, because of experimental difficulties, most of the corrosion rates available for metals in liquid fluorine are based upon very
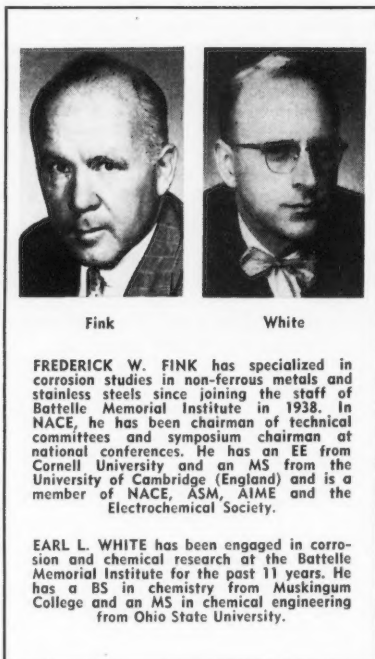
Fink **White**

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short periods of exposure and equilibrium rates were not reached. The satisfactory performance of such metals as Monel, nickel, and stainless steels in fluorine service indicate that much lower rates of attack can be expected than the rates which are obtained by short term exposure laboratory tests.

Figure 1 presents rate data developed by several investigators using short-term laboratory tests. These data indicate that a design engineer might select any of a number of different metals for handling fluorine. In many cases, the selection would probably be based upon factors other than corrosion resistance. Considering the fact that the corrosion rates decrease with time, the alloys of the heavy metals, such as nickel alloys, copper alloys, stainless steels, mild steel, and zirconium are all in the usable range. Tantalum, though it is attacked at just above room temperature, has a low rate of attack.

There are some objections to the use of certain of these metals. For example, the mechanical properties of steel are not so good as some other alloys at these low temperatures. It is reported that the fluoride film on stainless steels may tend to flake off and cause a "crud" problem in restricted flow applications. Even though Figure 1 shows a high maximum rate re-

Abstract

The corrosion behavior of materials of construction for handling liquid fluorine and liquid oxygen is summarized. This is an important matter in rocket construction. Even though both of these elements are very reactive, most of the common metals are sufficiently resistant for many applications. The compatibility with these oxidizers of alloys of iron, nickel, copper, aluminum, magnesium, titanium, and zirconium is discussed. Corrosion rate data compiled from both published and unpublished sources are presented. The compatibility of non metals and organic materials is also reviewed. Attention is given to the effect of initiating rapid reactions, or burning of both metals and organic materials by compressive impact, tensile impact, friction, wear, and other mechanisms.   4.7, 4.3.5

ported for Monel, it is probably the best metal, in most respects, for handling liquid fluorine.

Though the heavy metals probably are more resistant to fluorine, the missile designer may be more interested in the lighter materials for rocket applications.

Several of the light metals have been shown to produce protective films and be in the acceptable range of corrosion rates for rocket devices. Titanium, aluminum, and magnesium alloys can be considered for fluorine service (Figure 2). Though titanium and several of its alloys, such as the 6A1-4V alloy and the 8 Mn alloy, have shown low rates of attack, their usefulness still needs further study. It has been established that burning or explosion of titanium can be initiated by impact or other mechanical shocks under special conditions. However, it has been shown that this behavior is not reproducible and not limited only to titanium. In one experiment, for example, sensitivity was reported for a Monel pointed striker.

The danger of rapid reaction or burning of metals exposed to fluorine is not confined to titanium alone. Many metals and alloys probably can be caused to burn in fluorine. However, most often a primer of some sort is present to start the reaction. Organic materials under the proper

TABLE 1—Melting and Boiling Points of Selected Fluorine Compounds

Fluorine Compound	Melting Point, Degrees F	Boiling Point, Degrees F
CF₄	—299	—198
BF₃	—197	—150
PF₃	—256	—150
PF₅	—137	—121
SF₆	.....	— 83
SiF₄	.....	—141
Si₂F₆	.....	— 30
AsF₃	15	145
AsF₅	—112	— 63
TeF₆	— 31 subl.	.....
SeF₆	— 31 subl.	.....
WF₆	......	68
UF₆	......	133
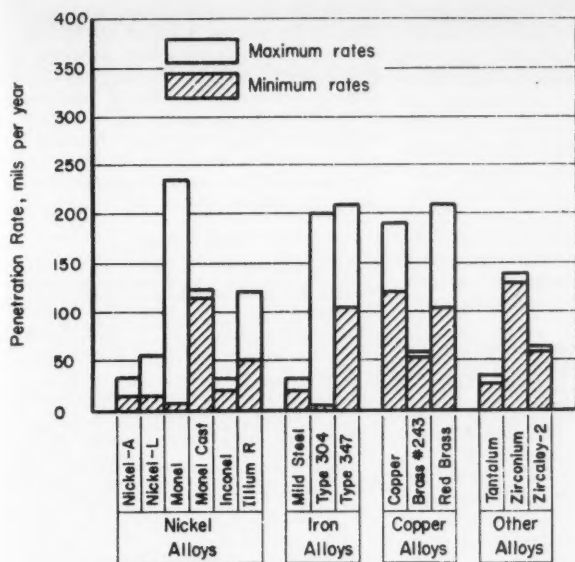
Figure 1—Corrosion rates of heavy metals in liquid fluorine at - 310 F.
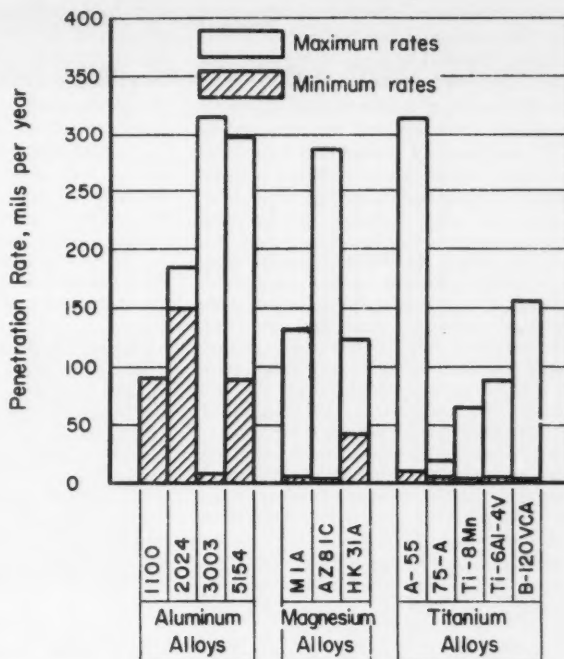
Figure 2—Corrosion rates of light metals in liquid fluorine at - 310 F.

conditions will spontaneously ignite in fluorine, and some inorganic materials also may react rapidly in fluorine. Therefore, any contaminating substance on or in a metal surface may act as a primer by burning and raising the temperature locally to the point at which the adjacent metal wall also will ignite. After ignition occurs, the reaction probably will continue until most all of either the metal or the fluorine has reacted.

Galvanic effects have not been thoroughly investigated. Some of the wide variation in results that are reported from similar tests suggests that galvanic coupling may accelerate the corrosion on one member of a couple. No instances of cracking or accelerated attack have, as yet, been traced to the effect of static stress. However, cyclic stressing or vibration may be sufficient to cause the fluoride film to be broken or spall and promote attack.

In using any material with fluorine, a pretreatment or conditioning treatment is recommended. Equipment for handling the fluorine, either gas or liquid, after first cleaning can be conditioned by exposing it at room temperature to a mixture of fluorine gas diluted with an inert gas. Under proper conditions, this treatment removes traces of contamination and initiates the formation of a relatively inert fluoride film. With the use of diluted gas there is less danger of encountering rapid reactions with traces of contaminants, though it is not a substitute for cleaning. This treatment will then permit the equipment to handle full strength fluorine, liquid, or gas.

Nonmetallic Materials

Almost all organic materials react spontaneously and violently with liquid or gaseous fluorine. The halogen-carbon compounds are the only exception. Though organic gaskets should be avoided wherever possible, Teflon or Kel-F can be used. Both materials are said to have poor cold flow properties and tend to change shape in gasket service.

Of the inorganic nonmetallics, alumina is resistant to fluorine, glass is suitable if no HF is present, asbestos may be used but it is difficult to clean. Other inorganic materials, not yet tested, may be found which will resist liquid fluorine.

As with metals, all nonmetallic materials must be thoroughly cleaned before contact with fluorine. Even very small amounts of combustible material may initiate burning. High flow rates over organic surfaces or high pressure operation also may contribute to ignition particularly of plastics. No impact tests of Teflon or Kel-F in fluorine are known, but these plastics may also be impact sensitive.

Corrosion by Liquid Oxygen (LOX)

Metallic Materials

Oxygen is a liquid at atmospheric pressure in the range of —361 F to —297 F. Though gaseous oxygen is considered to be a reactive material at elevated temperatures, oxygen in liquid form is considered to be noncorrosive. Most of the common metals are compatible with liquid oxygen. Stainless steels, nickel alloys, copper alloys, and aluminum alloys have all been used to handle the liquid. Silver solders are acceptable. Mild steel is not suitable because of its poor mechanical properties, rather than because of its corrosion resistance.

Titanium and titanium alloys deserve special consideration in connection with their use with liquid oxygen. Both titanium and its alloys are found to be impact sensitive under some conditions. It has been shown that, if an impact shock of sufficient magnitude is applied while the metal is immersed in liquid oxygen, a reaction may be initiated. These reactions can be very rapid or explosive. The local temperature of the metal surface may be raised to above its melting point. These reactions under certain conditions continue as long as the metal and liquid oxygen are in contact. It has been postulated but not positively proven, that to initiate the reaction, a gas phase is needed. In container service, titanium and its alloys are not readily fired by impact. They probably can be used in applications where suitable precautions are taken. Smooth surfaces are essential in this service.

Battelle and other organizations are investigating the mechanism of the reaction. It is expected when these studies are completed, that the conditions for the safe handling of LOX* will have been established.

As with fluorine systems, the thorough cleaning of liquid oxygen equipment is very important. The initiation of rapid reactions by more reactive primers occurs with oxygen as well as with fluorine. All oils and other organic contamination must be completely removed from the metal surfaces prior to exposure to liquid oxygen. Inorganic contaminants usually are not as reactive but also should be removed.

Nonmetallic Materials

Many plastics, elastomers, and even certain oils and greases do not spontaneously react with liquid oxygen. However, if energy is introduced into a system of an organic material and liquid oxygen, explosions or at least burning may occur. A variety of possibilities exist as to the sources of energy to initiate the reactions. Impact tests can be used to evaluate materials in an order of merit. Most of the

* Liquid oxygen missile grade.

testing procedures, which have been used for determining the sensitivity of LOX-organic material systems, have been of the compressive impact type. These tests usually consist of a drop weight apparatus in which a material can be immersed in LOX and struck a compressive blow with a falling weight. Many different organic materials have been tested by several investigators using variations of this type of equipment. It has been found that correlation of this type of impact sensitivity test results is difficult when a comparison is desired for test data obtained from different testing machines and operators. The results of impact tests from one machine may indicate the relative sensitivity of a series of materials, though they do not give a measure of the amount of energy which would initiate a rapid reaction in service. Both the cross sectional area of the striker which contacts the test material and the velocity of impact must be considered in comparing data from various testing machines.

Other sources of energy may also initiate reactions in operating equipment. Examples of this are: (1) heat produced by friction of metal surfaces, (2) heat from shearing of liquids, (3) heat generated by the catalytic breakdown of an organic material in contact with the metal surface, (4) adiabatic heating by compression of the gas phase over the liquid, (5) electrical discharge of static electricity produced by high velocity fluid flow, (6) shock waves, (7) violent heating by elastic or plastic deformation, and (8) the accumulation of heat from various sources because of the low thermal conductivity of materials at low temperatures. The effect of most of these energy sources has not been investigated. A battery of tests would be necessary to evaluate a material as to its compatibility with liquid oxygen under all foreseeable conditions.

The most reliable organic materials for LOX applications are the fluorinated organic compounds. And the more highly fluorinated the compound the more stable it is to attack by LOX. However, a large number of other organic compounds probably can be used in special applications. Until satisfactory testing procedures are worked out LOX must be treated as an explosive and any conditions which may introduce a high energy input to a system must be avoided.

Conclusions

Both liquid oxygen and liquid fluorine can be handled in most of the common construction materials. Stainless steels, nickel alloys, copper alloys, and aluminum alloys are all suitable for handling either of these liquids. Also, titanium alloys are probably suitable for many applications. Thorough cleaning of equipment is essential in handling either material. With either liquid oxygen or fluorine, organic materials should be avoided wherever possible but certain organics can be used to a limited extent.

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Practicality of Establishing Threshold Values
To Eliminate Stress Corrosion Failures in Metals and Alloys*

By HENRY SUSS

Introduction

CONSIDERABLE BASIC research and experimental work have been done in the last 15 to 20 years to obtain a better understanding of the stress corrosion cracking mechanism of metals. Work also has been done to determine the various factors which could contribute to a better understanding of the stress corrosion phenomena.

In this connection it is interesting to note:

1. There is a wide variation in test methods used to evaluate the stress-corrosion properties of metals and alloys. These tests have been performed by using U-bends, various modifications of bent beam specimens, or specially designed specimens to which stresses are applied by direct loading. The test specimens are exposed to simulated or accelerated type of corrosive media by localized wetting, partial immersion, total immersion, or alternate wetting and drying. There does not appear to be any universally acceptable stress corrosion test method.

2. Based on some of these different test methods, curves have been published by Logan and Hessing,[1] and by McGlasson and Greathouse,[2] which show a relationship between applied stress vs time to failure. A typical curve is the solid line in Figure 1. In addition Williams and Eckel[3] have issued a curve showing levels of oxygen and chloride below which austenitic stainless steel should not be susceptible to chloride stress corrosion cracking in alkaline phosphate-treated boiler waters.

Based on interpretation of the data in these curves, design, corrosion and material engineers have demonstrated considerable interest and effort in establishing threshold values for certain parameters, such as stress, concentration of corrosive ingredient, and/or temperature, below or above which a material should not be susceptible to stress corrosion failure in a finite period of time (desired life of a component).

Before definite opinions are offered on the practicality and advisability of establishing such threshold values, it is desirable to review some of the uncertainties as well as the pertinent factors involved which are directly or indirectly associated with the stress corrosion characteristics of metals and alloys.

1. Variations in tests:
a. Specimen (such as size, shape, and surface finish)

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b. Simulation of environment (corrosive media, temperature, stress, time, etc.; fixed and variable)
c. Measurement of attack, initiation and propagation of failure
d. Correlation to actual parts and service conditions.
2. Variations in materials (nominally within the same specification).
a. Inherent characteristics (chemistry, soundness, cleanliness, homogeneity, etc.)
b. Variable characteristics (residual stress, microstructure, mechanical properties, etc.).
3. Variations in design.
a. Stress concentrators
b. Size effects
c. Crevices
d. Inbuilt concentrations or galvanic cells
e. Reliability of protective coatings.
4. Variations in specimen and part fabrication.
5. Variations in actual service conditions.
6. Nature of corrosion attack (type of film formation; general or pitting attack).

Some of the available data on the above variables will be summarized in the following discussion. In the course of the review, references will be made to the effect of certain factors on fatigue life, and to acceleration of corrosion fatigue failures. These are included since the data are more complete and quantitative. It is recognized that many of the factors contributing to lowering the fatigue life will have a comparable effect on accelerating stress corrosion cracking. Similarly, data on sulfide corrosion cracking are included, even though many

Abstract

A review is offered on the significance of many factors which could affect the stress corrosion behavior of materials. These include such items as (1) method of test, (2) variations normally present in the materials conforming to the same specification, (3) slight variations in test environment or metallurgical structure of the metal, (4) accelerated corrosion attack (galvanic or crevice), (5) residual stress, and (6) nature of corrosion attack. Based on this review, it was evident that all the factors do not act independently; instead, there is a complex mutual interaction.

As a result of these factors, it has been concluded that the stress corrosion problem cannot be entirely eliminated at this time through control of specific parameters to established threshold values. The recommended approach is selection of an alternate resistant material. Other approaches to minimize the problem are proper design, reduction of the corrosivity of the environment, reduction of effective stress, or use of a protective layer. Evaluation under actual service conditions is an essential requirement. The possible danger of localized failure or increasing porosity of a protective layer with continued exposure of the base metal also is emphasized.

Special attention is given in this study to the behavior of AISI 410 steel.   3.5.8

attribute this type of attack to hydrogen embrittlement rather than stress corrosion cracking.

Reproducibility of Curves

Very little work has been done on determining the reproducibility of such threshold curves. Variations may occur among different heats of the same material within the same test media. At present, the data are not complete on material prone to stress corrosion failure that is exposed for very long periods of time under low stress or conditions of low corrosion rates. These additional data could change the shape of the curve. Recent unpublished data showed that the
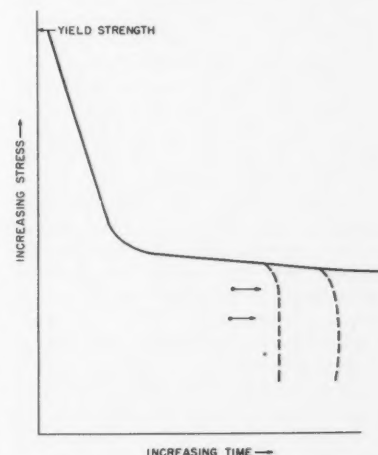
Figure 1—Stress vs time to failure.

curve in Figure 1 changed its shape to that of the dotted lines for hardened (RC36-42) AISI 410 exposed in a marine atmosphere.

Effect of Experimental Conditions

H. L. Logan has performed considerable laboratory studies on the stress corrosion properties of magnesium alloys in accelerating environments. He reported[4] that "Work in his laboratory and elsewhere showed that the reported threshold values were procedure-sensitive. It was considerably higher if specimens were loaded in tension before the corrodent was added, than if the specimens were already immersed in the corrodent when the stress was applied. While a threshold stress was readily obtainable in laboratory experiments, such a threshold stress has not been observed in weather exposure tests, most probably because the specimens were also subject to general corrosion. Furthermore, there was little difference in average times to failure for a given stress, whether specimens were exposed in marine atmospheres at Hampton Beach, Va. or in urban atmospheres at the Bureau.[(1)] It was noted that most failures occurred during or following rain." Logan[4] offered an explanation for the latter phenomena.

Staehle, Beck and Fontana[5] testing susceptibility of austenitic stainless steel in 400 F chloride waters, showed a very wide range in results. The range depended on whether specimens were fully immersed during the exposure or subject to intermittent wetting and drying. In the latter instance failures occurred with stresses and chloride content as low as 2000 psi and 50 ppm, respectively. In the former condition, there were no failures until the chloride content was increased to 20,000 ppm and stress levels raised as high as 35,000 psi. Increasing the chloride content from 40,000 ppm to 80,000 ppm did not indicate any stress corrosion failure with applied stresses as high as 80,000 psi.

Cornet and Golan[6] have studied the effect of temperature on corrosion fatigue life of steel wire and compared their results with results of similar tests performed by Gould[7] and Fink, Turner, and Paul.[8] The results reported showed wide variation among experimenters. The extremes were such that Cornet and Golan's data showed (with applied stress of 45,000 to 75,000 psi) increasing fatigue life with increasing temperatures from 80 F (27 C) to 180 F (83 C). Gould's data (with failure at 10M cycles) showed decreasing fatigue life, with increasing temperature 15 C (59 F) to 45 C (113 F). Cornet and Golan felt that differences were due mainly to experimental methods in exposing samples to the corrosive atmospheres. Their test specimens were fully immersed, while Gould used a drip device to corrode only a small part of the wire. The writer feels that differences could be attributed also to variations in lots and/or chemistry of the wires used by the experimenters.

(1) National Bureau of Standards, Washington, D.C.

Effects of Variations in Chemistry in Corrosive Media

The ASM Review,[9] in abstracting a German paper by Spindler,[10] reported: "Stress-corrosion resistance of AlMg[r] and Al-Cu Mg alloy was tested in various aqueous solutions of metal chlorides. The composition of distilled water used proved very important in that even slight changes in the content of metal ions showed strong effects. Chlorides of alkali metals, alkaline earth metals and earth metals do not cause stress-corrosion unlike chlorides of Cu, Hg, Fe, Co, Ni, Sn, Pb, and Cd."

Ferric chloride ($FeCl_3$) is a known corrosion product resulting from the exposure of iron-bearing materials (carbon, low alloy, and stainless steels) to chloride environments. Edeleneau[11] reported that additions of ferric chloride to sodium chloride and magnesium chloride solutions resulted in considerable acceleration of stress corrosion attack of austenitic stainless steels. Uhlig and Lincoln[12] felt that the presence of ferric chloride was the basis for the increasing corrosivity of a used magnesium chloride solution. The latter was a reagent used for some of the accelerated stress corrosion tests of austenitic stainless steels.

Studies have been conducted at KAPL[(2)] and BAPL[(3), 13] on the susceptibility of AISI 410 (hardened to RC 36-42) to stress corrosion attack in high-temperature high-purity water. They showed that in low-oxygen (0.5 to 2 ppm) water at 300 F, there was considerably more pitting and stress corrosion attack with applied stresses as low as 60,000 psi, when compared to those exposed under same conditions with applied stresses as high as 80,000 psi in high-oxygen water (30 to 40 ppm) at 300 F. No data are available on intermediate oxygen levels. It is very probable that the high-oxygen environment passivated the surface and eliminated or decreased the corrosion attack. The author feels that the extent of oxygen required to produce passivation is a function of temperature for a specific corrosive environment, decreasing with increasing temperature. It is essential, therefore, to evaluate the relationship of oxygen content for each environment and temperature as to accelerated corrosion attack or passivity.

Effect of Metallurgical Factors

Test data[13] evaluated at KAPL showed that variations existed among heats of AISI 410 in their apparent susceptibility to stress corrosion cracking. Samples from three heats (H-1, H-2 and H-3, Tables 1 and 2) were evaluated. The chemical composition and mechanical properties after heat treatment[(4)] are shown in Table 1 and 2 respectively. Heat H-2 showed variations in residual

(2) KAPL—Knolls Atomic Power Lab. Operated by General Electric Co. for the Atomic Energy Commission.
(3) Bettis Atomic Power Lab.—Operated by Westinghouse Electric Co. for the Atomic Energy Commission.
(4) Austenized at 1800 F, cooled to room temperature, and then tempered at 650 F for two hours.

molybdenum and a lower tensile strength, but these did not appear to be of significance. For the studies, the three heats were exposed to air saturated water[(5)] at 300 F, with applied stresses from 40,000 to 80,000 psi. All samples of heat H-1 and H-3 failed in two weeks or less. After 8 weeks' exposure, none of the samples from H-2 indicated any apparent failures on visual examination at 30X. Metallographic studies of samples H-1 and H-3 as heat-treated, showed the structure typical of as-quenched and tempered low-carbon alloy steel (see Figure 2). The cracks which developed on exposure of all specimens of H-1 and H-3 were typical intergranular cracks, as can be seen in Figure 3.

Heat H-2 indicated similar structure, except for the presence of longitudinal stringers of delta ferrite and smaller former austenitic grain size (see Figure 4). Sample H-2 after 8 weeks of exposure in air saturated water with applied stress of 40,000 psi, indicated slight micro cracks (see Figure 5). The propagation of these cracks had been stopped by presence of the delta ferrite grains. Exposure with applied stress of 80,000 psi, Figure 6, produced considerably more cracking below the surface. Crack propagation appears also to have slowed down by the presence of the delta ferrite grain. This effect by delta ferrite grains is better shown in Figure 7, supplied by Crucible Steel Corporation.[14]

Based on studies at KAPL, Crucible Steel Corp., and comments on the latter paper, it was apparent that the presence of delta ferrite in hardened AISI 410 will increase the time for crack initiation at a specific applied stress. It also will slow down crack propagation whenever the crack has to deviate (because of a delta ferrite grain) from a path which is normal to the direction of the applied stress, and will not stop crack propagation whenever the crack moves in a direction parallel to the grain flow.

Fraser and Eldridge[15] remarked that as a result of studies on available data on sulfide corrosion cracking "the test procedures used in the past were largely qualitative as were the conclusions which were drawn from them. Nevertheless they are sufficiently quantitative to show that steels which are nominally of the same chemical composition and mechanical properties (e.g., API Grade N-80 steel) may vary widely in susceptibility to cracking."

The tempering temperature has a pronounced effect on the susceptibility of such materials as martensitic stainless steels (such as AISI 410) to stress corrosion cracking. Test data have revealed that AISI 410 shows susceptibility or immunity to stress corrosion cracking on tempering below or above 1050 F respectively. Limited studies by the author[13] have shown that the basis for immunity of the material tempered over 1050 F could be attributed to changes in metallurgical structure, relieving of any stresses which may have developed as a result of prior heat treatment and/or phase change, and the nature of pit formation

(5) Details of conditions in item 13, Bibliography.
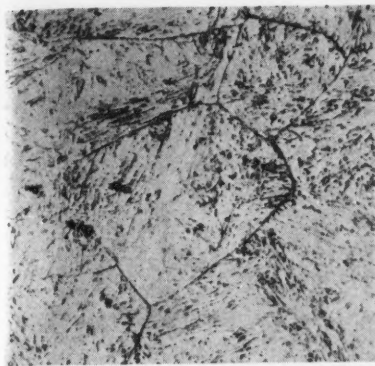
Figure 2—AISI 410 specimen austenized at 1800 F, air cooled and tempered at 650 F for two hours. Typical heats H-1 and H-3. Vilella's reagent, 770X.

Figure 4—AISI 410 specimen austenized at 1800 F, air cooled and tempered for two hours at 650 F. Heat H-2. Vilella's reagent, 770X.
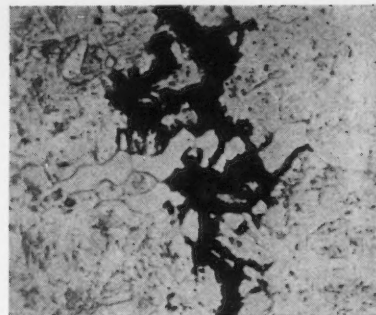
Figure 6—Same as Figure 5 but with applied stress of 80,000 psi. Vilella's reagent, 770X.
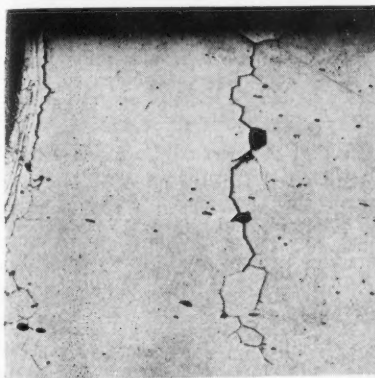
Figure 3—Typical intergranular stress corrosion crack in AISI 410 tempered at 650 F. Oxalic acid electrolytic, 37X.
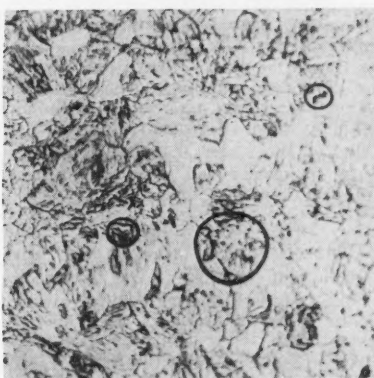
Figure 5—Same as Figure 4 but for specimen exposed eight weeks in air saturated water at 300 F with an applied stress of 40,000 psi. Slight micro cracks are circled. Vilella's reagent, approximately 770X.
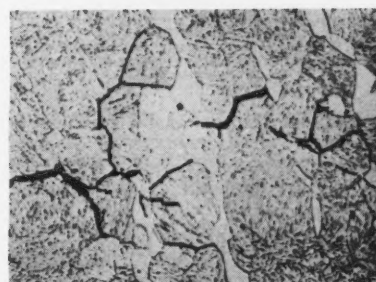
Figure 7—AISI 410 sample oil quenched from 1800 F, tempered at 900 F and exposed 30 days to 5 percent NaCl with applied stress of 70,000. Five percent picral plus 5 percent HCl etch, 770X.

(rounded pits 1125 F—sharp pits at 650 F). The significance of the nature of pit formation will be discussed later in this report.

Effect of Mechanical Properties

Warren and Beckman[16] studied the sulfide corrosion cracking of high strength (AISI 4140) bolting material. Their observations indicated:

(1) In absence of plastic deformation, no bolt failures occurred at hardness levels below RC 27, even under stresses approaching the yield strength of the material. In the hardness range of RC 27-55, the cracking susceptibility increased with increases in the hardness and applied stress. For each hardness there appeared to be a minimum or threshold stress required to produce cracking. Increasing hardness lowered the minimum stresses to failure. Some typical data on stress to failure as function of hardness are:

		(approx.)
RC-30	....	49,000 psi
35	....	22,000 psi
40	....	12,000 psi

The above data clearly show that slight changes in hardness will show a considerable change in the required tensile stress for failure. The significance of these data is enhanced with realization that material from the same heat that was heat treated at the same time, could show variations of 2 to 3 points in hardness.

(2) In addition, plastic deformation and the accompanying residual stresses increased susceptibility to sulfide corrosion cracking, by lowering the minimum hardness for absence of cracking to RC 22. It also increased the number of bolt failures at hardnesses of RC 27-33.

Nature of Surface Corrosion Attack—Pitting

Mears[17] advises that contrary to general opinion, localized corrosion attack is probably the form to be expected rather than general corrosion attack. This becomes more apparent since most commercial metal and alloys are polycrystalline, and contain areas of dissimilar phases to a greater or lesser degree. Corrodents will have the tendency to attack specific areas preferentially (localized pitting attack), and the resultant electrochemical reaction will promote accelerated attack in these specific areas to the exclusion of the adjacent areas.

The extent and nature of the pitting attack can be of significance in promoting or accelerating the stress corrosion attack. Fontana's[18] stress corrosion studies of AISI 403 (410) showed that the material reveals variation in type of pitting attack as function of tempering temperatures. Sharp pitting attack was evident

TABLE 1—Chemical Composition of Heats

Heat	ELEMENT										
	C	Mn	P	S	Si	Cr	Ni	Mo	V	W	Al
H-1	0.12	0.56	0.022	0.011	0.41	12.23	0.27	0.07	0.07	0.05	0.005
H-2	0.10	0.63	0.027	0.028	0.33	12.71	0.32	0.32	0.05	0.05	0.003
H-3	0.15	0.70	0.024	0.010	0.30	12.20	0.34	0.03	0.04	0.05	0.002

TABLE 2—Mechanical Properties of Heats

Heat	Tensile Strength, psi	Yield Strength 0.2 Percent Offset, psi	Elongation 2 in., Percent	Reduction in Area, Percent	Rockwell Hardness C
H-1	192,000	140,000	9.3	62.3	42
H-2	182,750	141,750	15.0*	60.3	39
H-3	199,300	139,160	9.3	57.9	41

* Three-in. gage length.

Figure 8—Bare AISI 410 sample austenized at 1800 F, cooled to 550-600 F and tempered at 1140 F for four hours. Sample was exposed to air saturated water at 300 F for four weeks. Turbo chrome etch, 250X.
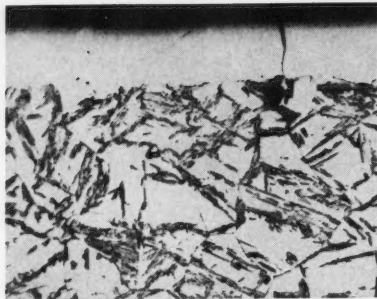
Figure 9—Chrome (0.002 inch) plated over AISI 410. Heat treatment and exposure are same as in Figure 8. Turbo chrome etch, 250X.

Figure 10—AISI 410 in contact with Stellite 6. Heat treatment and exposure are as in Figure 8. Vilella's reagent, 180X.

in material tempered at 650 F. The radii at the base of pits increases with increasing tempering temperature, to a point where rounded pits are evident on tempering over 1100 F. Sharp pits act as stress raisers, which, together with the applied stress, produce localized highly stressed areas to accelerate stress corrosion failure. Although the sharpness of pitting decreases, stress corrosion failure still occurs with material tempered as high as 1000 F.[19] AISI 410 tempered between 800 F and 1000 F (blue brittleness range) results in a more brittle, notch sensitive material. Corrosion will initiate pitting. The degree of sharpness of the root of the pit is indicative of the extent of the localized stress raiser. Crack initiation and first stages of crack propagation to failure will be a function initially of the combined localized and applied stress. The time interval to final mechanical failure will be a function of the notch sensitivity of the material. This notch sensitivity effect in the stress-corrosion failure of high-strength steels was studied by B. F. Brown.[20] Some of his pertinent observations were:

1. If a notch sensitive material is subjected to a high tensile stress in service, and a notch is introduced, the specimen could rupture more rapidly and at much lower stress than anticipated. A stress corrosion crack might be expected to produce such a notch. In this instance, a purely mechanical failure may terminate a stress corrosion crack and give an erroneous impression of rate of stress corrosion cracking.

2. If a similar stress is applied to a material that is not notch sensitive, it would have to undergo a great deal more of stress corrosion attack, until the stress produced by the crack exceeded the net fracture stress.

3. Some metals exhibit a transition from ductile to notch sensitive condition when the test temperature is lowered sufficiently. Also the transition temperature is strongly dependent upon such metallurgical variables as composition and heat treatment, and thickness of the specimen.

Nature of Surface Corrosion Attack

Oxide Film Formation

A significant factor in a material's corrosion resistance properties in a specific environment, is the presence and nature of the surface oxide film formed before or during an exposure. The protective value is dependent upon the film's adherence, absence of porosity, resistance to deformation under conditions of exposure (applied or residual tensile stresses), ability to repair any damage prior to any significant corrosion attack, and chemical resistance to the specific environment. Failure of a film in localized areas, with a resultant exposure of the base metal could set up an electro-chemical reaction. Since the base metals are generally anodic, this could be an ideal situation for accelerated galvanic corrosion attack. (Logan[4] and Leu and Helle[21] have discussed film formation characteristics in more detail.)

Boiling of Corrosive Media

Some systems are designed to eliminate boiling, but in some instances complete absence of boiling cannot be assured. Wanklyn and Jones[22] have presented a discussion of the effects of boiling in accelerating the extent of corrosive attack.

1. Heat is removed less rapidly from a surface covered by steam than from one in water. The alternate formation and removal of steam bubbles will cause rapid local fluctuations in the temperature of the oxide film on the metal. These fluctuations might crack the oxide film by thermal shock and reduce its protective value, leading to increased corrosion or pitting attack.

2. Secondly, austenitic stainless steels can be subject to transcrystalline stress corrosion cracking when exposed to concentrated solutions of chlorides or caustic, even though the concentration of these constituents is low in the bulk water. Higher concentrations develop in the "concentrating films"[(6)] under each bubble, so that over a long period, all areas of the surface (in contact with the boiling solution) can be exposed to an aggressive solution.

Furthermore, concentration of solutions could occur in components containing crevices or other constricted areas which are subjected to heat-transfer conditions.

(6) Wanklynn and Jones[22] advised that Hall[23] has described a method whereby solids are concentrated at the interface of a steam bubble by contact of water and a heat transfer surface.

This concentration of a solution in restricted areas has contributed to many chloride and caustic stress-corrosion failures of austenitic stainless steels.

Effect of Accelerated Corrosion Attack

Studies at KAPL[13] on AISI 410 have shown that conditions of exposure which produce galvanic or oxygen concentration cells will accelerate stress corrosion cracking without any visible general corrosion attack. Additional studies[24] further confirmed this fact.

Bare AISI 410, chromium plated (0.5 to 2.0 mils) AISI 410, and bare AISI 410 in contact with Stellite 6 (cobalt base alloy) were exposed to 300 F air saturated water[(7)] with stress of 60,000 psi. The AISI 410 was in a condition prone to stress corrosion failure. The very slight surface and intergranular attack on bare AISI 410 is shown in Figure 8. Accelerated intergranular cracking in the chromium-plated sample (directly under cracks which exposed the base metal), and in contact with the Stellite are shown in Figures 9 and 10 respectively.

Residual Stresses or Stress Raisers[(8)]

In analyzing a design, knowing the loads, it generally is possible to calculate the nominal applied stresses or stress fluctuations in critical areas. It could simplify the problem, if these calculated stresses were the "true" picture as to total stresses (tensile) or stress distributions. Unfortunately there are many factors which cannot be observed or predicted in advance, and which can be of significance in the over-all stress picture. These factors are residual stresses, and/or stress raisers. Measurement or analyses of these localized stresses or stress patterns are often very difficult to make. The highly localized stress concentrations can become a significant factor in the over-all analysis of many stress corrosion studies. It is the author's opinion that many of the wide variations or anomolous results on stress corrosion studies

(7) Demineralized water (1.0 to 2.0 meg-ohm resistivity) air saturated at room temperature. Details in Reference 13, Bibliography.
(8) Residual Stresses are defined as all stresses remaining after an external load has been removed.

can be attributed directly to variations in the nature or extent of the residual tensile stresses or the presence of stress raisers. These can be present originally in the material, or introduced in some phase of sample preparation and fabrication, design, and/or handling.

A Bureau of Aeronautics report[25] had a discussion on certain factors which contributed to build up of the localized residual stresses or stress raisers, and their effect on fatigue life. Pertinent data follow:

(1) "A point of interest is that fatigue cracks tend not only to start at faults and inclusions or stress raisers in a metal, but often will propagate along lines from one fault to another."

(2) "Geometric discontinuities in sections are perhaps the most obvious stress raisers, since such discontinuities clearly cause changes in stress patterns. It should be noted that there are other types of discontinuities which may be considered stress raisers. Surface roughness may give rise to very localized variations in stress. Inhomogeneities in a metal (porosity, inclusions, etc.) are sometimes considered "metallurgical stress raisers." Some of these discontinuities cause local changes in stress on account of changes in elastic modulus rather than, or in addition to, changes in the load bearing section. With some, there are associated other factors (local variations in yield point, residual stresses, etc.) which may influence fatigue strength in addition to the influence of stress concentration."

(3) "Non-metallic inclusions at or near the surface of an alloy steel or aluminum will reduce the fatigue strength. It is, however, difficult to determine the quantitative loss in fatigue life, because much depends on the type and location. The type of inclusions that are most harmful are those oriented normal to the direction of loading. Inclusions in fillets or at other geometric discontinuities, and inclusions at the surface are most harmful. Long longitudinal inclusions may not be too harmful. If a fatigue crack does start at an inclusion, it will tend to progress from one inclusion to another. Highly heat-treated steels are particularly sensitive to inclusions, but the soft steels are relatively insensitive."

Other sources of residual stresses and potential stress raisers are listed below. The significance of some of these items will be reviewed.

1. Cold forming or straightening, without a subsequent full-stress relief.

2. Quenching stresses as a result of thermal gradients, and/or results of increasing volume produced by such a phase change as transformation of austenite to martensite in steels.

3. Welding stresses (absence of final stress relief treatment). Test work at KAPL showed an interesting effect of welding stresses.[26] Stress corrosion cracking tests of Type 347 steel were conducted at 636 F for periods up to 1800 hours with 1- and 4-molal solutions of sodium hydroxide. A capsule specimen (consisting of 1-inch schedule 40-pipe and welding caps) containing the solu-

tions was studied as a test method to evaluate susceptibility to caustic cracking. The design of the capsule, the internal pressure, and nature and extent of a highly stressed area are shown in Figure 11. Stressed U-bend samples were included in the solution. Eight out of eight capsules, not stress-relieved after welding, failed in the welds and welded regions (both in the upper area subject to wetting and steaming, and the lower area fully immersed) by transgranular cracking in approximately 100 hours. Two out of four capsules with stress-relieved welds failed in a thin-wall gage section at a stress level of about 22,000 psi. One out of eight U-bend specimens (not stress-relieved) failed. It is apparent that the as-welded stresses were at least equivalent to the yield strength or higher. It is possible that the crevice created by the backing plate could be a "concentrating area" and may have accelerated the failures. This crevice is not the significant factor, since it did not promote failure of the stress relieved weld joints.

4. Operating temperature gradients and presence of dissimilar metals with different coefficients of thermal expansion can produce both static or dynamic stress conditions. This can accelerate stress corrosion failures as well as other modes of failures such as creep, stress rupture, or corrosion fatigue.

5. Plastic deformation caused by service conditions or resulting from testing (hydrostatic pressure or thermal cycling).

6. Notches or sharp corners introduced by machining or subsequent handling.

7. Distortion of misalignment of threads during assembly or in service.

8. Poor machining techniques(such as use of dull tools, improper grinding wheels or improper coolants).

It is the writer's opinion that localized residual tensile stresses are of greater significance to the stress corrosion problem than an equivalent uniform applied tensile stress. It is possible that, in a corrosive environment, areas of high localized tensile stresses can set up an electrochemical reaction with the adjacent low or compressively stressed areas to promote localized corrosion attack. The subject of potential and possible reversal of the potential, as effected by localized tensile and compressive stresses, was discussed in a recent paper by Yang, Horne and Pound[27] and in many of the discussions of this paper.

Discussion

Stress-corrosion cracking requires the presence of both corrosion attack and tensile stresses. If it was possible to control either, it could be possible to establish limits for the other, below or above which stress corrosion attack should not occur. Based on the above review, it is apparent that both the corrosion process and the actual tensile stress within a member are greatly dependent on various factors. These do not act independently. Actually, there is a complex mutual interaction among the specific factors affecting corrosion and stress.

Therefore, the suggested principle of attempting to establish specific param-
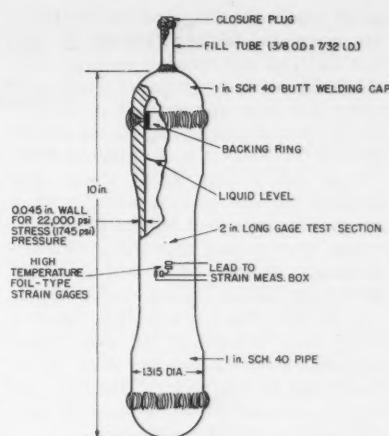
Figure 11—Capsule test specimen (caustic stress corrosion cracking).

eters below or above which stress corrosion failure will not occur is believed impractical at this time. If it is attempted, it may prove to be unsafe.

Alternate Approaches

The use of alternate corrosion resistant materials is the desired method of eliminating the stress corrosion problem. If alternate materials are not available, other approaches can be considered and evaluated such as:

1. Designing parts to eliminate or minimize factors which could promote stress corrosion attack.

2. Eliminating surface tensile (applied or residual) stresses.

3. Eliminating corrosion attack through the use of protective layers or inhibitors of the corrosive environment.

A brief discussion of each follows.

Designing Against Stress Corrosion

Good design practices, some suggested in a paper by Phelps,[28] are a practical approach to minimize (but not completely eliminate) stress-corrosion failure. These practices include avoiding crevices, deep recesses, dissimilar metals, sharp corners, and notches. They also include keeping geometric discontinuities to an absolute minimum, avoiding the possibility of plastic deformation during product testing, assembly, and in end use, avoiding careless handling of work-hardenable and high strength (notch sensitive) material, and avoiding design which could produce high thermal stresses as a result of changing temperatures in the intended service. Also, when residual stresses are a possibility, stress relief treatments should be included as part of the processing procedure. In this instance, it must be determined that the temperature of the stress-relief treatment will not cause distortions or changes in mechanical properties beyond that which can be tolerated.

Eliminate Tensile Stresses

One of the more successful methods of eliminating stress corrosion failure is substituting a compressive layer on the surface to counteract any applied or re-

sidual tensile stresses. Residual compressive layers can be accomplished by surface rolling and/or shot peening. The writer has recently prepared a report,[29] which has been summarized in *Steel*,[30] on a limited successful application of shot peening for protection of hardened AISI 410, in 300 F high purity water. The adoption of any process introducing a compressive layer will require prior evaluation to determine that the service environment, anticipated stresses, nature of stress (constant or cyclic), and temperature of the exposure will not cause a reduction or fadeout of the surface compressive residual stresses. Also, there should not be any problem for most application in establishing adequate process and quality control procedures.

Eliminating or Reducing Corrosion Attack

Protective Layers

The application of a protective layer would be a desirable approach to minimize or eliminate corrosion attack. Each system must be completely evaluated to be sure that the protective layer remains completely adherent, is crack and porous-free under conditions of end use (such as temperature, changing temperature, or applied stress), and is resistant in the anticipated environment. Localized failure or porosity which exposes the base metal could cause accelerated stress corrosion cracking as shown in Figure 9. Studies reported by the writer[13] have shown that a chromium plate which cracked in test and exposed the base metal produced accelerated stress corrosion failures under conditions in which unplated material did not fail.

Cathodic Protection

In cathodic protection, a current in conjunction with an anode is impressed on the part to convert it into a cathode. This will eliminate corrosion attack on the part. At the cathode, hydrogen, which is continuously discharged, can readily saturate the material. Under these conditions, metals can be subjected to accelerated failure, if they are susceptible to hydrogen embrittlement. Such failures were reported in comments by Dr. Mears at a recent Stress Corrosion Symposium.[31] He reported: "With a small amount of cathodic current, the cracking time is lengthened" (but not eliminated) —"indicating that cathodic protection is obtained. At high cathodic current densities, however, relatively short cracking times are observed, which indicates that hydrogen embrittlement is obtained." Cathodic protection is not recommended to reduce corrosion attack (especially ferritic steels) for the elimination of stress corrosion failures.

Inhibition of the Corrosion Media

Inhibition can be defined as a method of chemical addition or controls which will reduce the corrosivity of the medium, or act as a scavenger for a corrosion or stress corrosion accelerator.

Properly controlled chemical treatments of boiler waters have markedly reduced the problem of caustic embrittlement of steels and chloride stress corrosion cracking of austenitic stainless steel components. Numerous studies of treatments and specific inhibiting compounds have been conducted and adopted by the chemical and petroleum industry. Inhibitors or systems have been developed for specific applications. General over-all inhibitors, however, are not available. Before a specific inhibitor is adopted, complete evaluation is necessary under actual service conditions (not accelerated laboratory tests) to determine the inhibitors compatibility, anticipated service life, necessary controls, and applicability to a specific design concept. This is especially true if crevices or deep blind recesses are present.

Conclusions

The evidence in this report shows that a complete solution to the stress corrosion problem cannot be guaranteed through controls of certain parameters and establishing threshold values, (on such items as temperature, stress level, and corrosion rates) above or below which stress corrosion failures will not occur. A safer, and recommended, approach is to use an alternate resistant material. It is possible to minimize the stress corrosion problem by careful attention to all pertinent design, materials, environmental, production and service variables.

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DISCUSSION

Question by A. V. Alessandria, Arabian American Oil Co., New York, N. Y.:

Examples were given of stress corrosion cracking of heat treated Type 410 stainless steels with metallic protective coatings which were cathodic to the Type 410 steel. Has any work or information been developed on the effect of anodic type coatings on stress corrosion cracking of Type 410 steel?

Reply by Henry Suss:

All tests on stress corrosion properties of AISI 410 were performed in high temperature (300 F) high purity waters. In these environments, typical anodic type coatings (zinc, tin, and aluminum) have very poor corrosion resistance properties. Therefore, no studies were conducted. Dr. E. H. Phelps presented a paper in which he reviewed some data on successful use of anodic coatings for protection of steels against stress corrosion failures.* Also, when anodic type coatings are used for corrosion protection, hydrogen is evolved at the cathode, the part being protected. Susceptibility to hydrogen embrittlement should be evaluated for the material of interest with the desired anodic coating, under actual or simulated environmental conditions and temperature.

* E. H. Phelps and A. W. Loginow. Stress Corrosion of Steels for Aircraft and Missiles. *Corrosion*, 16, 325t (1960) July.

Effect of Flow Rate on the Galvanic Corrosion Of Low-Carbon Steels in Sea Water*

By EINO UUSITALO

Introduction

IN PREVIOUS studies[1-3] of the corrosion of low-carbon steels used in ice-breaker construction, the author found that in the cases where the corrosion of the welded seams had been pronounced, the weld metal was strongly anodic relative to the ship plate. This fact was clearly established by corrosion potential measurements which yielded reproducible data.

A special apparatus[3] was developed for comparative potential measurements in which electrodes prepared from different steels could be exposed simultaneously under constant conditions to an electrolyte solution flowing at a fairly high rate (up to 5 m/s) past the electrodes. As shown by separate experiments in which the temperature and the oxygen content of the solution were varied, the corrosion potential of a steel in sea water is very sensitive to the amount of oxygen at the surface of the steel. In the experiments carried out to date the flow rates have been kept constant.

The flow rate has, however, a great influence on the corrosion of steels in oxygen-containing electrolytes as it determines the diffusion of oxygen to the steel surface and the removal of the corrosion products. An increase in the flow rate promotes the corrosion of steels by galvanic micro cells in both ways[4, 6] and hence it can be expected also that the corrosion in galvanic macro cells formed between different steels will be augmented by the flow of the electrolyte. The clarification of the effect of flow rate on the galvanic corrosion is of great significance in explaining the cor-

★ Submitted for publication September 18, 1959.
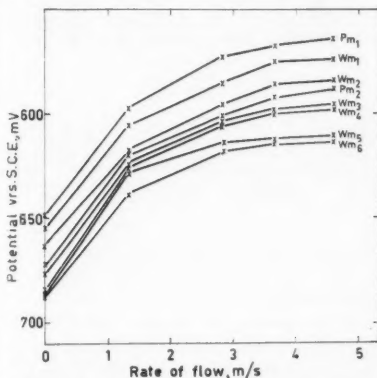
Figure 1—The effect of flow rate on the corrosion potentials of some low-carbon steels in sea water at 0 degrees C. The potentials were measured after immersion for six days. Graphs from top to bottom are as follows: Pm₁, Wm₁, Wm₂, Pm₂, Wm₃, Wm₄, Wm₅, Wm₆.

About the Author

EINO UUSITALO served as research and instruction assistant at the Finland Institute of Technology, Helsinki and as corrosion researcher in the employment of the Corrosion Section of the Central Chemical Association, Helsinki. He has a Doctor of Technology degree in physical chemistry from Finland Institute of Technology, Helsinki.

rosion of hulls of ships and other metals subjected to high rates of flow.

Experimental

The experiments were performed in the same manner as in the earlier studies. Eight electrodes of identical size and form made from different steels were fastened to a 25 cm rod insulated by a plastic tube through which a connecting lead led to each electrode; the soldered joints were completely isolated from the electrolyte solution. The electrode assembly was placed symmetrically into the cylindrical vessel (diameter 30 cm, height 35 cm) containing the electrolyte. The electrode shafts were fastened with screws to the cover of the vessel which in turn was fastened water-tight to the vessel itself. The electrodes were placed with their largest surfaces parallel to the walls of the electrolyte vessel. The electrolyte solution was brought to flow at a high constant rate past the electrodes by means of a rotating horizontal plastic plate to which plastic vanes were attached. By altering the speed of the motor turning the plastic plate from 0 to 400 rpm, the rate of flow of the elec-

Abstract

The effect of flow rates ranging from 0 to 5 meters per second on the galvanic corrosion of low-carbon steels in sea water at 0 degrees C has been studied by: (1) recording current-potential curves of the steels, and (2) measuring the potentials, current strengths and weight losses of galvanic cells formed by the steels in pairs. The corrosion of the steels forming galvanic cells was found to be up to 15 times as great at high rates of flow as in standing sea water, but the variation of the flow rate did not alter the order of nobility of the examined steels.

3.6.6, 6.2.3, 4.6.11, 3.6.11

trolyte solution at the surface of the electrode could be varied between 0 and 5 meters per second.

The electrolyte, an artificial sea water, was maintained at a temperature of 0 degrees C and was allowed to absorb oxygen freely through its exposed upper surface. The solution was prepared by dissolving the following chemically pure reagents in one liter of distilled water: $NaCl$-28gm, $MgCl_2 \cdot 6H_2O$-5gm, $MgSO_4 \cdot 7H_2O$-7gm, $CaCl_2 \cdot 6H_2O$-2.3gm and $NaHCO_3$-0.2gm.

The electrodes were prepared from the metals in question by machining rectangular rods to the dimensions 30x15x2 mm at one end and to the dimensions 20 mm long and 2 mm in diameter at the other end, the latter end to be used for fastening. Heating of the electrodes during and after the machining was carefully avoided. The edges of the electrodes were rounded and the final polishing performed with sand paper, grade 00, before use and before each new series of measurements.

The chemical treatment of the electrodes prior to their immersion in the electrolyte proved to be a very decisive factor, especially when the measurements were made using standing water or low rates of flow. If the oxide layer on the surface is not removed, the attainment of a reproducible condition by the electrodes takes much longer than when the oxide layer is removed chemically prior to the immersion. The oxide layer was removed by treating the electrodes first with dilute hydrochloric acid (0.5 N) and then quickly with distilled water, care being taken not to allow the electrode to become oxidized again.

TABLE 1—Compositions of the Investigated Low-Carbon Steels.*

Abbr.		ELEMENT				
		C	Si	Mn	P	S
Wm₁		0.071	0.07	0.68	0.01	0.018
Wm₂		0.070	0.15	0.45	0.01	0.018
Wm₃	Weld metals with	0.072	0.29	0.62	0.01	0.019
Wm₄	varying silicon content	0.080	0.31	1.37	0.01	0.012
Wm₅		0.067	0.68	0.78	0.01	0.014
Wm₆		0.073	0.54	1.00	0.013	0.017
Pm₁	Parent metals with	0.24	0.04	0.56	0.004	0.030
Pm₂	increasing silicon content	0.14	0.16	0.99	0.031	0.039

* Pm: Rolled ship plates, Wm: Weld metals rapidly cooled from the melt.
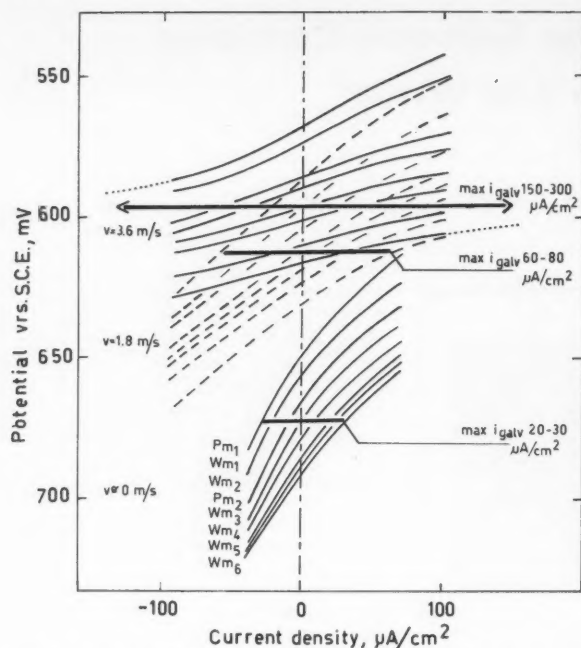
Figure 2—The effect of flow rate on the current-potential curves of low-carbon steels immersed in sea water at 0 degrees C. Measurements were made during 2 hours at each location after the electrodes had been immersed 5 days.
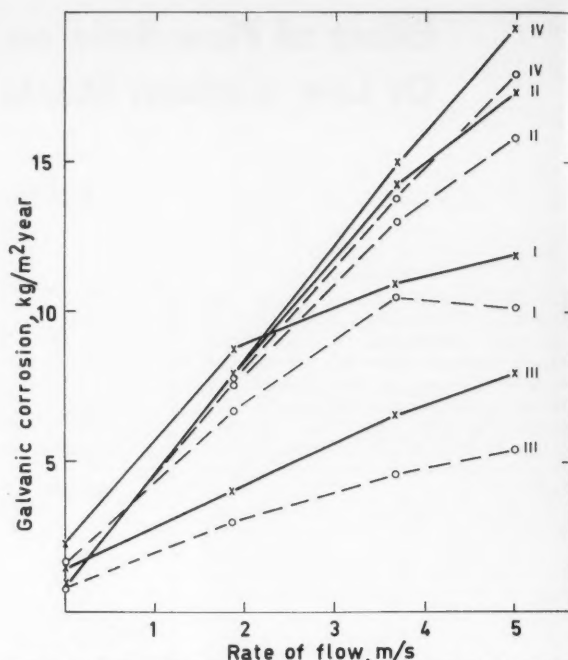
Figure 3—The corrosion of steel anodes in galvanic cells as calculated from current measurements during six days (o mark on graph) and from weight losses during the whole duration of the experiment (x mark on graph). For the nature of electrode pairs I-IV see text.

The reference electrode employed in the potential measurements was a saturated calomel electrode. The side tube of the electrode ended in a capillary tube whose open end was located opposite the steel electrode at a set distance from the latter and parallel to the direction of flow of the electrolyte solution.

The corrosion potentials of the steel electrodes were measured relative to the calomel electrode with a precision potentiometer after they had become constant; this usually required one week after the electrodes had been immersed in the flowing electrolyte solution.

The polarization curves of the steels in the electrolyte solution were measured under the same conditions as the corrosion potentials. In these experiments a saturated calomel electrode with a large exposed surface was placed in the solution in addition to the reference electrode to conduct the required polarization currents.

After the potential and polarization measurements had been performed, the steel electrodes were connected in pairs, e.g. a plate metal and a weld metal or two weld metals, by external leads. The potential of each pair of electrodes and the current flowing in the cell were measured daily during several days. The current strengths were determined by inserting a small precision resistance in the circuit of the electrodes and measuring the drop in potential across the resistance with the potentiometer, and by applying Ohm's law. When the experiment had ended, the potentials of the electrodes were measured once again immediately after the electrodes had been disconnected. The electrodes were finally cleaned, dried and weighed to determine their loss in weight.

The low-carbon steels examined are presented in Table 1.

Effect of Flow Rate on Corrosion Potentials

The potentials of steel electrodes selected for study were measured after they had been immersed 4-6 days in flowing sea water. The results obtained at various flow rates are given in Figure 1. It will be noted that the order of nobility of the steels has remained unaltered over the range of variation of the flow rate although the potentials have changed from 70 to 90 millivolts in the more noble direction. Furthermore, the potential differences are seen to be somewhat greater at high rates of flow than in standing sea water. The weld metals seem to become slightly less noble relative to the plate steels as the flow rate increases.

Effect of Flow Rate on Current-potential Curves

The current-potential curves of the examined steels at different flow rates are plotted in Figure 2. At the same time as the potentials of the steels change in the more noble direction with increasing flow rate, the slopes of the curves decrease. This is readily understood since the diffusion of the oxygen to the corroding surface, which reduces the polarization at the cathode surface, is facilitated by the higher flow rate.

It is further seen from the current-potential curves that no changes in the order of the nobility of the steels have occurred in the studied range of current densities although the current-
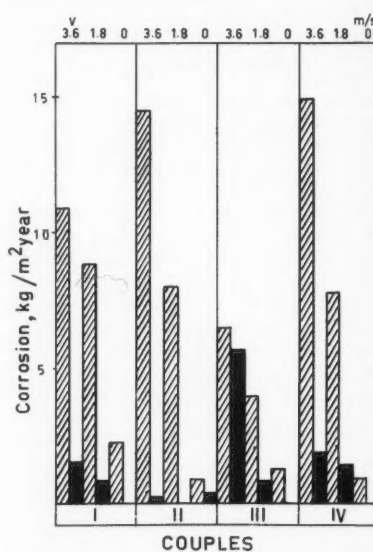
Figure 4—The corrosion of anodes and cathodes in galvanic cells of low-carbon steels in sea water at 0 degrees C flowing at different rates. Diagonal lines indicate corrosion of the anodes and black areas the corrosion of the cathodes. For the nature of electrode pairs I-IV see text.

potential curves of the more noble steels possibly have slightly smaller slopes at high current densities.

By drawing a horizontal line between the polarization curves (see Figure 2) so that the distances along the line from the vertical zero current axis to the pair of curves are equal, it is possible to determine approximately the strengths of the currents passing through galvanic cells
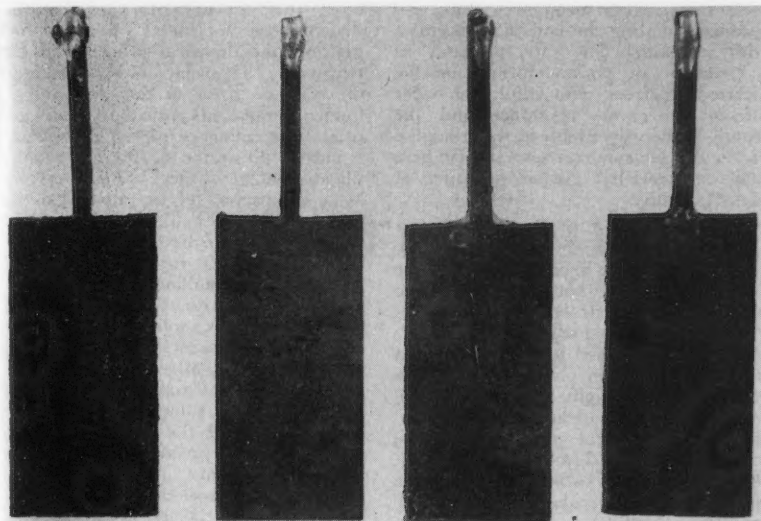
Figure 5—Photographs after 10 days of surfaces of two pairs of steel electrodes forming galvanic cells in sea water at 0 degrees C, flowing 3.6 meters/second. The anodes are outermost and the cathodes innermost. The potential difference between the electrodes after they were disconnected was 85 mV for the electrode pair on the left and 60 mV for the pair on the right. The corrosion rates expressed as weight losses are, from left to right: 280, 0, 55 and 420 mg/dm² day.

Galvanic cell I : anode, weld metal W^m_3
cathode, weld metal W^m_1
II : anode, weld metal W^m_6
cathode, weld metal W^m_2
III : anode, weld metal W^m_4
cathode, parent metal
P^m_2
IV : anode, weld metal W^m_5
cathode, parent metal
P^m_3

The corrosion currents passing through the galvanic cells were determined by measuring potential drops over a resistance of 2 ohms to which the electrodes were connected in pairs.

The rates of corrosion of the anode electrodes as calculated from current measurements during six days and on the other hand from the weight losses during the whole time of galvanic contact in the conditions mentioned above and at various flow rates are shown in Figure 3. The corrosion is seen to have increased greatly in all cells with increasing flow rate. Pryor and Keir[7] have obtained similar results in a study of the effect of flow rate on the galvanic corrosion between some aluminum alloys and steels. A comparison of the current and weight loss data shows that they are very well correlated in the cases where the galvanic effect has been great, but that the corrosion current was relatively low in case III where the galvanic effect was weak.

Weight losses of both anode and cathode electrodes in the galvanic cells I-IV mentioned above during ten days' exposure to sea water flowing at different rates are shown in Figure 4. The rates of corrosion of both anodes and cathodes increased greatly with the flow rate. A change in the flow rate from 0 to 3.6 meters/second has effected a 10-15-fold change in the rates of corrosion of the electrodes functioning as

formed by the pairs of electrodes in question. In this way it is found that, as the flow rate increases, the galvanic corrosion current increases to many times its initial value in standing sea water. Thus, for instance, the current passing through the cell formed by the most noble and least noble steel (Figure 2) was 20-30 μ Amp in standing sea water but

150-300 μ Amp at the highest flow rate employed.

Effect of Flow Rate on Properties of Galvanic Cells

The effect of flow rate on the properties of galvanic cells formed by the steels was studied not only by recording the current-potential curves but also by measuring potentials, currents and weight losses in the following galvanic cells with the artificial sea water as electrolyte:
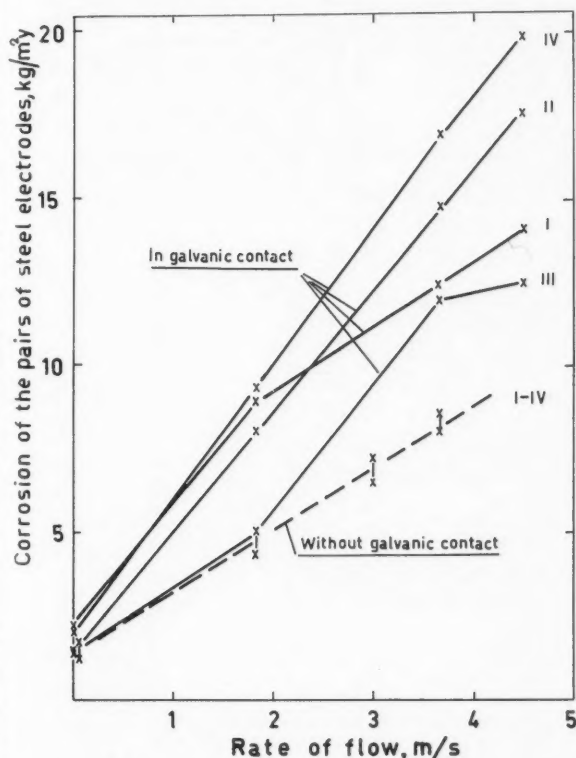
Figure 6—The relation between the corrosion of low-carbon steels with and without galvanic action, in sea water at 0 degrees C flowing at the rates 0-4.5 meters/second.
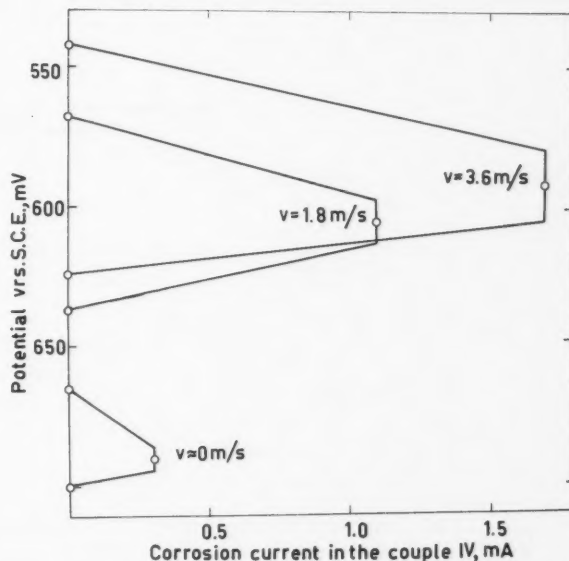
Figure 7—Schematic presentation (Evans' triangles) of the properties of a galvanic cell formed by two low-carbon steels in sea water (0 degrees C), flowing at different rates.

anodes. The corrosion of the cathodes has been weak compared to the corrosion of the anodes except in case III where the galvanic effect was weak. In standing sea water the steels that have been the anodes have provided the cathodes a strong cathodic protection.

Photographs of the electrodes of two strong galvanic cells I and IV after 10 days are reproduced in Figure 5. The cathodes are seen to have become almost completely covered by a gray layer of oxide, especially in the pair shown at the left where the anode has offered the other electrode cathodic protection but has itself corroded strongly. The photographs as well as weight losses indicated for the cells I, II and IV reveal the effect of a strong galvanic cell which leads to a rapid distintegration of the anode while the cathode remains practically unaffected.

Weight loss data given in Figure 6 show the corrosion of the steel pieces selected for study in sea water flowing at different rates with and without a superimposed galvanic effect. From the figure it is seen that the corrosion of the pairs of electrodes has been greater when they have formed galvanic cells than when they have been isolated from each other. The corrosion of the couples was limited almost entirely to the anodes in the strong cells (Figure 4) and hence the corrosion of these electrodes was very great.

The nature of the corrosion is illustrated by Evans' triangles for different flow rates (see Figure 7). From these triangles it is seen that the corrosion of steel under the chosen conditions is cathodically controlled with greater polarization on the cathode in standing sea water, but that this control diminishes as the flow rate increases. At the highest flow rates the corrosion is about equally controlled anodically and cathodically. The effect of the ohmic resistance (the vertical line in the triangle represents the potential drop over ohmic resistance) limiting the corrosion increases with increasing flow rate, probably as a result of air pockets formed on the electrode surfaces. The salinity of water affects the ohmic resistance and the length of the vertical line in the triangles. Hence the galvanic corrosion studied here may be somewhat greater in water of higher salinity.

Discussion

Examples of the high rates of galvanic corrosion of low-carbon steels exposed to high rates of electrolyte flow are provided by the welded seams of icebreakers which have corroded in some cases to a depth of 3-5mm in one year. This corresponds to a weight loss of 640-1050-mg/dm² day. The highest rates of corrosion measured in the present study have varied between 1.3 and 2.0 mm/year, but the anode and cathode surfaces were equal in area in the experiments, whereas in icebreakers the ratio of cathode and anode surfaces has been many times greater (in cases where the welded seams have corroded). An increase in the cathode area leads to a greater corrosion at the anode area.[8,9] It is, of course, true that ships are not always in motion and the corrosion rate is lower when they are in port. The present results do, however, show that the galvanic corrosion of the same grades of steel has been of the same order of magnitude in both practical and experimental conditions.

The results of the present study show that the same steels in different galvanic pairs have been anodes in all experiments where the flow rate of the electrolyte was varied, but the corrosion of the steels functioning as the anodes increased greatly when the flow rate was increased.

The factors that primarily determine the potential differences between the examined steels and which thus promote the galvanic corrosion of the steels are those that determine the crystalline structure of the metal (namely, composition, metallurgical process and heat treatment). These factors also determine the state of stress of the steel and the foreign components present in small quantities. The influence of the latter factor is clearly illustrated by the effect of the silicon content of steel. This is revealed by a comparison of the analytical data for the steels in Table 1 and the corrosion potentials of these steels in Figure and by the data for the corrosion of pairs of steels combined in galvanic cell in the other figures. It will be seen that the steel is less noble the higher its silicon content, provided that the proportions of the other components are approximately the same. This means that the higher the silicon content of the plate metal and the lower the silicon content of weld metal the greater is the corrosion resistance of welded seams because anodic corrosion of seams decreases when the potential of the weld metal becomes more noble relative to the potential of plate metal.

The silicon content of the steel is not the sole affecting factor influencing the corrosion.

Similar observations were made with respect to other components, but there is no reason to present these results here because the influence of the flow rate was very similar in all cases. The effect of these other components in different qualities of low-carbon steels will be discussed in more detail in another paper.

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**Any discussion of this article not published above
will appear in June, 1961 issue.**

Symposium on

Corrosion of Iron and Tin

Five papers presented at the Symposium on the Corrosion of Iron and Tin at the Southeastern Regional Meeting of the American Chemical Society, Richmond, Virginia, November 6, 1959. Other papers not reproduced here also were a part of the original symposium.

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Accelerated Corrosion Test for Tin Plate In Grapefruit and Other Juices*

By P. R. CARTER and T. J. BUTLER

Carter   Butler

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Introduction

RESEARCH IN the area of tin-plate corrosion by various canned food products has been hindered by the extreme length of time necessary for obtaining food-pack results. To overcome this difficulty, many accelerated tests[1] and interesting electrochemical experiments[2] have been proposed. The disadvantage of such tests is that they are usually performed in synthetic media, and hence any correlation obtained with actual pack performance is an empirical one. Also implicit in this approach is the assumption that tin-plate quality is ranked in the same order in all products of interest. A recent paper,[3] showed, however, that the corrosion mechanism in grapefruit juice and in tomato juice is considerably different from that in prunes.

Kamm et al[4] have recently devised the alloy-tin couple (ATC) test, an accelerated test to determine the corrosion performance of tin plate in citrus products. In this test, specimens of tin plate detinned to the alloy layer are coupled to a tin anode in grapefruit juice through a low-resistance current-measuring system. The galvanic (ATC) current thus measured correlates well with the pack performance of the tin plate. Low currents in testing indicate good performance and high currents show poor performance.

The authors' work at the U. S. Steel Applied Research Laboratory has paralleled that of Kamm, and the initial success of the ATC test prompted an investigation to determine the possibility of using the technique as a corrosion test in other foods. The results of this investigation, together with the results obtained in a study of numerous ATC test variables, are the subject of the present paper.

Experimental

Standard Test Conditions and Preparations

The experimental procedure is essentially the same as that described by

★ Submitted for publication May 3, 1960.

Abstract

Investigation of an alloy-tin couple (ATC) test described by Kamm and associates indicates a good correlation between ATC current and grapefruit juice pack life. The effect of Sn(II) additions to the electrolyte, of the source of the tin anode, of variations in sample and anode area, of resistance of the external and internal circuit, and of scratches on the sample surface is discussed. Increasing alloy-layer thickness decreases the ATC current. ATC measurements made in grapefruit, tomato, and pineapple juices rank various lots of tin plate similarly, but in prune juice a different ranking is observed. This difference is consistent with previous data, which showed the mechanism of corrosion of tin plate for grapefruit and tomato juices to be different from that of prune juice.   8.3.5, 6.3.14

Kamm[4] except for a few minor changes in the design of the test cell, of the tin anode, and of the current-measuring system. The cell, shown in Figure 1, consists of three parts: a 2-liter glass jar, a tight-fitting micarta lid, and a tin anode. The lid has 10 openings, through which the samples are admitted to the test solution. Each of the samples has a test area of 3.6 square centimeters (sq cm) and is coupled to a common sheet-tin anode (Fisher Scientific Company, purified grade), 0.015 inch thick, with an area of approximately 600 sq cm.

The test solution for one cell is prepared from two cans of a frozen concentrate of sweetened grapefruit juice, diluted 1 part of juice to 3 parts of distilled water, and a sufficient quantity of reagent-grade stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) so that the Sn(II) concentration is 100 parts per million (ppm). The solution is boiled for about 2 minutes to deaerate and to sterilize it, and is then allowed to cool to test temperature under a stream of oxygen-free nitrogen. This nitrogen flow is maintained for the duration of the tests.

The method of sample preparation is the same as that described by Kamm[4] with the exception that beeswax instead of microcrystalline wax is used as the masking material to form the test area (3.6 sq cm).

Since the ATC current is temperature dependent, the test must be conducted at constant temperature (near room temperature). If a thermostatically controlled room is not available, a constant temperature box similar to the one shown in Figure 2 is recommended (21 in. wide by 17 in. deep by 15 in. high). A temperature of 30 C has been selected for this work, except when temperature is a test variable.

Since the test solution is susceptible to bacterial spoilage, care must be taken to sterilize the test cell, the lid, and the sample holders by either boiling them in water or heating them in a drying oven. Contaminated equipment may cause the juice to spoil in less than a week as indicated by the evolution of numerous bubbles of gas, probably CO_2, from the solution. With the above precautions, the test solution should last for the recommended three weeks.

Electrical Circuit

Current measurements are made on an electronic galvanometer, Kintel Model 204A, Figure 2, which is very insensitive to shock and vibrations. Because the high

Figure 1—Test cell.

MICARTA LID

N₂ INLET

SOLUTION LEVEL

GRAPEFRUIT JUICE

SPECIMEN

TIN ANODE

OIL

N₂ OUTLET

H₂O
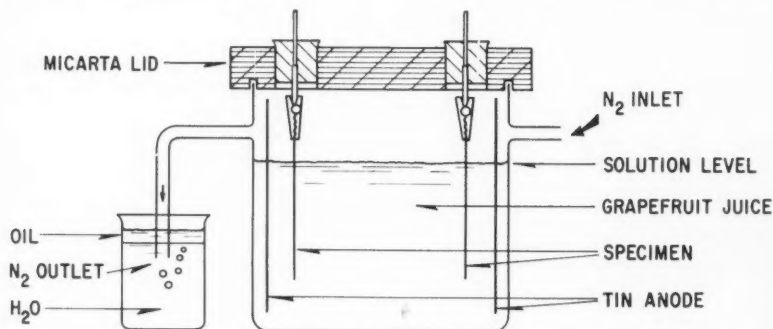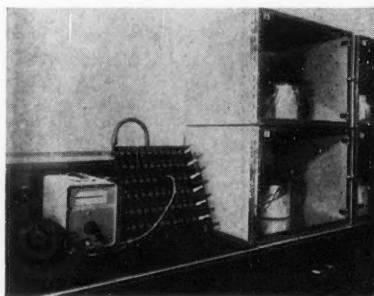
Figure 2—Current-measuring system.
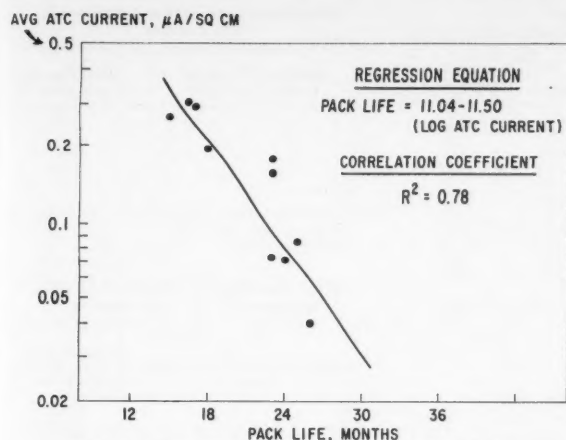
Figure 3—Comparison of average ATC current and pack life.
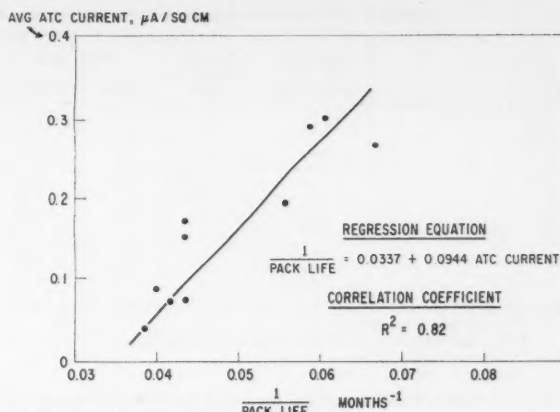
Figure 4—Comparison of average ATC current and pack life. Reciprocal of pack life is used as the abscissa.

TABLE 1—Effect of Stannous Ion Additions* and Age of Juice on ATC Current

	ATC Current, μ amp/sq cm										
	0 ppm Sn (II)			50 ppm Sn (II)			100 ppm Sn (II)			200 ppm Sn (II)	
	Day of Test			Day of Test			Day of Test			Day of Test	
Sample**	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd
A-1	0.22	0.08	0.07	0.09	0.05	0.09	0.08	0.04	0.04	0.03	0.02
B-1	0.81	0.33	0.30	0.30	0.29	0.21	0.31	0.26	0.22	0.18	0.15
C-1	0.30	0.12	0.12	0.09	0.12	0.06	0.08	0.07	0.10	0.05	0.04
D-1	0.70	0.64	0.40	0.43	0.33	0.38	0.38	0.27	0.29	0.25	0.20
E-1	0.77	0.33	0.30	0.31	0.29	0.23	0.28	0.28	0.21	0.15	0.11
Average	0.56	0.30	0.24	0.24	0.22	0.19	0.23	0.18	0.17	0.13	0.10

* Added as $SnCl_2 \cdot 2H_2O$.   ** Selected to give a range of test values. Duplicates were run on each of the three days.

resistance (10,000 ohms) of the galvanometer makes it inadvisable to measure the current directly, the instrument is used as a microvoltmeter to measure the voltage across a known resistance (28 ohms) in the circuit. The ATC current is then calculated from the equation

$$ATC \text{ current} = \frac{voltage}{area \times resistance}$$

Since results to be described later indicate that the circuit resistance is not critical, a convenient resistance can be chosen to make the product of area and resistance equal to some multiple of ten so that the meter scale can be read directly in microamperes per square centimeter (μ amp per sq cm).

Electrical leads in shielded cable from the test specimens and the tin anode terminate in short-circuiting telephone jacks mounted on a panel board near the galvanometer, Figure 2. The leads from the galvanometer terminate in a cable plug, which, when inserted into the telephone jack, makes the circuit through the galvanometer before it breaks the short circuit between the tin and the sample. The plug is inserted in turn into each jack and the current readings are recorded.

Test Specimens

In general, the tin-plate samples in each study were selected to give a range of test values and in all instances represented experimental lots.

Test Variables Studied

Although grapefruit juice containing 100 ppm Sn(II) is the standard test solution, in one set of experiments various concentrations of Sn(II) were added to the grapefruit juice to show the effect of Sn(II) on the ATC current.

In other experiments, solutions of pineapple juice, tomato juice, and prune juice, each containing 100 ppm Sn(II), were used as the test solution. For these test media, the pineapple juice was prepared from a frozen concentrate; the tomato juice and prune juice were commercial brands packed in glass bottles. Temperature was also a variable in these experiments.

Normally, all 10 samples in a given cell are coupled to the same large tin anode. In experiments where the tin-anode size was varied, however, individual anodes were coupled to each sample. This was done by placing the anode and the sample through adjacent holes in the lid of the cell. The exact area was masked off by waxing around small plastic forms.

In experiments on the effect of circuit resistance on ATC current, the external resistance was changed by varying the resistance of the shunt across the galvanometer. The internal resistance (that is, the circuit resistance through the solution) was changed by varying the distance between the electrodes and by varying the size of the anode. The internal resistance was measured on an alternating-current (1000 cycles per second) bridge.

Alloy-Weight Variations

The variation in alloy weight was ob-

tained by varying the current in the resistance melting unit.

Results

ATC Current and Grapefruit-Juice Pack Life

The data in Figure 3, which show a plot of log ATC current versus grapefruit-juice pack life for lots that have all been tested in the same grapefruit-juice pack, indicate that a good correlation exists. A plot of the same data with ATC current as the ordinate and the reciprocal of pack life as the abscissa, Figure 4, gives a correlation at least as good. Each point on the graph represents the average of a minimum of 40 cans for pack life and of at least 15 ATC values. In other instances, where packing variables are not minimized or where relatively few cans or ATC values are used, poorer correlations are obtained.

Effect of Sn(II) Additions to the Electrolyte

Although under proper conditions the test juice can be used for three or four weeks without bacterial spoilage, the dissolution of the tin anode may result in day-to-day variations in the tests result. Tin additions to the test solutions minimize this variation and would shorten the time necessary to obtain a constant current. Table 1 shows the effect of Sn(II) additions and of the age of the juice on the ATC current of miscellaneous samples. In general, the test values on the first day are higher than those obtained on duplicate samples on subse-

TABLE 2—Dissolution of Iron and Tin During the ATC Test

Juice	Nominal Sn (II)* Added, ppm	Age of Juice,** Days	Iron, ppm		Tin, ppm	
			Initial	After Test	Initial	After Test
A-2	70	21	1.5	2.4	67	185
B-2	70	22	1.4	2.2	65	170
C-2	100	9	1.3	1.7	102	125
D-2	50	7	***	1.7	***	85
E-2	0	3	0.7	1.4	6	27
F-2	200	2	1.5	1.0	164	202
G-2	100	20	***	1.4	***	133
H-2	100	20	***	1.2	***	134
I-2	100	20	***	1.2	***	129
J-2	100	20	***	1.5	***	130
K-2	100	5	***	1.0	***	108

* Added as SnCl₂ · 2H₂O.
** Number of days that test specimens were in the juice.
*** Not analyzed.

TABLE 3—Effect of Tin Anodes From Different Sources on ATC Current

Sample	Average ATC Current,* μ amp/sq cm		
	Commercial Tin	Alkaline Tin	Ferrostan Tin
A-3	0.04	0.03	0.04
B-3	0.03	0.03	0.04
C-3	0.16	0.14	0.17
D-3	0.08	0.09	0.09
E-3	0.35	0.36	0.37
Average**	0.13	0.13	0.14

	Commercial Tin	Tin Plate***
G	0.37	0.36
H	0.28	0.30
I	0.26	0.24
J	0.20	0.26
K	0.10	0.12
Average	0.24	0.26

* Average of triplicates run on three days.
** The daily average did not differ from this average by more than ± 0.02.
*** Anode cut from tin plate from which the test specimen was prepared. Its area equaled the area of the test specimen.

TABLE 4—Effect of Anode Size on ATC Current

Ratio of Tin Area to Sample Area*	ATC Current, μamp/sq cm
¹⁄₁₂	0.20
⅙	0.20
⅔	0.19
¼	0.21
½	0.20
1½**	0.23

* Sample size 3.6 sq cm.
** Normal ratio.

TABLE 5—Effect of External Circuit Resistance* on ATC Current

External Circuit Resistance, ohms	Average** ATC Current, μ amp/sq cm
280	0.188
65	0.182
28	0.208

* Internal resistance is 35 ohms.
** Twenty measurements per average.

quent days, particularly when Sn(II) is not added initially to the solution. Also the test values average lower for the higher initial concentration of Sn(II). Although these data do not conclusively indicate the optimum initial concentration of Sn(II), experience has shown that a concentration of 100 ppm Sn(II) results in a satisfactory test solution, which was adopted as the standard test solution. The high values on the first day indicate that the juice should be aged before use.

Analysis of the data in Table 2 shows that very little iron is dissolved during the test. These data indicate that the dissolved tin must therefore come from the anode and not the alloy (FeSn₂) test specimen and that the test specimen is almost completely cathodically protected. The relatively large increase in tin concentration in the juice is undoubtedly due to small quantities of air entering the cell when test specimens are replaced.

Effect of Sn Anode Source

The data shown in Table 3 indicate that the source of the tin from which the tin anodes are made does not affect the ATC current. The commercial tin (the usual anode) is the Fisher Scientific Company purified grade. The alkaline and the Ferrostan tin are high-purity grades prepared electrolytically at the Laboratory from an alkaline stannate and from the Ferrostan tin-plating bath (phenolsulfonic acid, stannous sulfate), respectively.

The tin-plate anodes were cut from plate from which the test specimen was prepared, and each sample was coupled with an individual tin-plate anode. The values obtained show that the substitution of tin plate for tin as the anodic material in the ATC test does not affect the ATC current. This would imply that the current measured in the ATC test between pure tin and the alloy-layer specimen could be of the same order as the galvanic current generated between the tin coating and the underlying alloy-layer-covered steel base.

Other Factors Affecting ATC Current

In general, the galvanic current in a couple is controlled by the open-circuit potentials of the electrodes, by the polarization characteristics of the electrodes, and by the resistance of the entire electrical circuit.[5] Data presented in Tables 4-7 indicate that in the ATC test the polarization of the test specimen is the controlling factor in determining the ATC current.

Table 4 shows that the relative size of the tin anode, and hence its polarization, is not a controlling factor in determining the ATC current. Tables 5 and 6 show that increasing the circuit resistance by a factor of 4 or 5 has only a slight effect on the ATC current. Table 7, however, shows that the total galvanic current is almost proportional to the test-specimen area, but that the current density is reasonably constant.

Occasionally a few specks of tin (probably much less than 1 percent of the test area) will remain on a specimen even after a prolonged period in the detinning bath. The data in Table 8 indicate that this small amount of tin does not signifi-

cantly affect the ATC current. This fact is an aid in preparing samples for the test and is consistent with the finding that the resistance of the circuit is not a significant factor in determining the ATC current. The amount of current shunted to the adhering tin coating should be proportional to the ratio of the areas of the adhering tin and the anode. Large areas of adhering tin will therefore reduce the ATC current.

The fact that (1) the alloy layer has a high hydrogen overvoltage[6] and (2) increasing the alloy-layer thickness decreases the ATC current (see subsequent section), leads to the conclusion that for a given tin plate the ATC current is an indication of the porosity of the alloy. That is, it is an indication of the amount of steel base exposed through the alloy. Table 9 shows that the observed ATC currents for varied steel areas exposed increase proportionally with increasing areas of steel exposed, and are in good agreement with the values calculated by considering the relative contributions from the exposed steel areas and the areas covered with alloy. This would indicate that samples slightly scratched inadvertently during preparation could be tested without fear of spurious results. However, deep scratches that gouge the metal may lead to abnormally high ATC currents.

If the magnitude of the ATC current is governed solely by the porosity of the alloy layer, it would have to be assumed that for a sample with an ATC current of 0.1 μ amp per sq cm and a base-metal ATC current of 1.0 μ amp per sq cm, the alloy layer would have to be porous to an extent that 10 percent of the base metal is exposed (see Table 9). This seems to indicate a very high porosity.[7] Also, if porosity is the controlling factor, breaking the brittle alloy by fabricating the plate into cans or by deforming the plate[8] should lead to higher porosity and hence to higher ATC currents. The data in Table 10 do not support this assumption. Specimens from cans and from deformed plate gave on the average about the same ATC currents as plate not so treated. The data in Tables 9 and 10
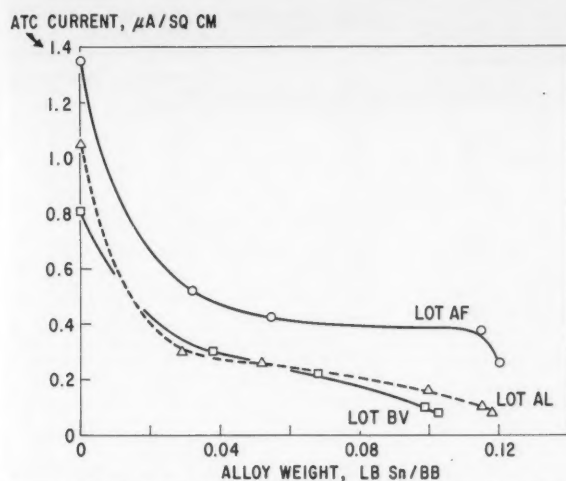
Figure 5—Effect of alloy weight on ATC current for three lots of tin plate.
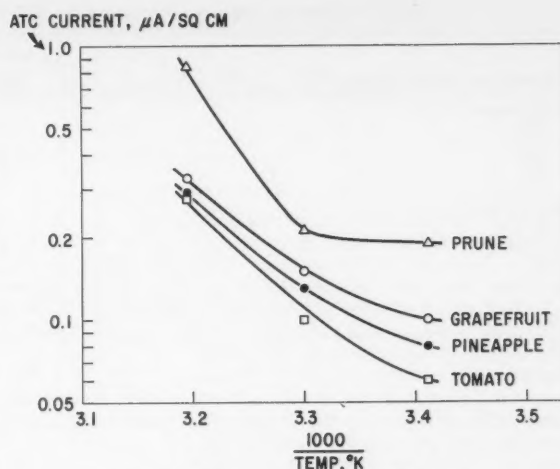
Figure 6—Effect of temperature on ATC current.

TABLE 6—Effect of Electrical Resistance on ATC Current

Sample	Internal Resistance,* ohms	ATC Current, μ amp/sq cm	
		28 ohms**	280 ohms**
A-6	74.5	0.11	0.10
A-6	107.5	0.10	0.09
B-6	74.5	0.25	0.22
B-6	110.0	0.26	0.23
C-6	85.0	0.31	0.28
C-6	122.0	0.32	0.29

* Measured on a 1000-cps bridge.
** External circuit resistance.

TABLE 7—Effect of Test Area on ATC Current

Test Area, sq cm	ATC Current,* μ amp/sq cm		Total Current, μ amp	
	Sample A	Sample B	Sample A	Sample B
1.2	0.08	0.50	0.10	0.60
2.4	0.06	0.54	0.14	1.29
3.6	0.07	0.53	0.25	1.91
7.2	....	0.56	....	4.03

* Average of duplicates.

TABLE 8—Effect of Incomplete Detinning on ATC Current

Sample	ATC Current, μ amp/sq cm Area of Tin Remaining	
	None*	Trace**
A-8	0.02	0.02
B-8	0.06	0.05
C-8	0.16	0.15
D-8	0.48	0.42
E-8	0.07	0.06

* Normal preparation.
** Less than 1 percent of the test area.

imply that either the alloy layer is much more porous than is suspected or some other factor also plays a prominent role in determining ATC currents. It should be noted, however, that Hoare[8] was working with hot-dipped tin plate, the alloy of which is very heavy and would be more susceptible to fracture under his experimental conditions (bending over a ¾-inch mandrel) than the alloy of the electrolytic tin samples listed in Table 10.

One may conclude that it is not necessary to take unusual precautions in sample preparation, and that studies of more severe deformation, as a function of alloy weight, similar to that given tin plate in the side-seam areas should be undertaken.

Effect of Alloy-Weight Variation on ATC Current

The data showing the effect of alloy-coating weight on ATC current are listed in Table 11. A plot of these data, Figure 5, shows that ATC current decreases with increasing alloy weight. In most instances, the relationship between these two variables can be described as a sharp decrease in ATC current when matte tin plate is melted, followed by a region of decreasing slope (sometimes an actual plateau), followed by a region of increasing slope. This decrease in ATC current with increasing alloy weight has also been demonstrated for tin plate that has been remelted to produce increasing alloy weights following an initial melting and quenching operation.

The lots listed in Table 11 have been packed in grapefruit juice. Preliminary results indicate that there is a substantial difference in pack life between matte and melted plate, but that the additional benefit anticipated for the heavier alloy weights has not been obtained. This is the first serious evidence of a lack of correlation between grapefruit-juice pack life and ATC current, a discrepancy that is not presently understood.

If the ATC current is simply a measure of the porosity of the alloy, then one would expect a smooth, continuous relationship between ATC current and alloy weight similar to that shown by Kerr[7] for a plot of porosity versus tin-coating

weight rather than the plateau so frequently observed. As pointed out earlier in this paper in connection with the data shown in Table 9, porosities ranging up to 30 percent would be necessary to explain the observed ATC currents.

Much of the evidence presented has suggested that the alloy serves simply as a barrier layer, and the more effectively it covers the steel base, the lower the observed ATC values. Other evidence somewhat circumstantial, suggests that the answer is more complex. For example, sizeable differences in porosity would be necessary to explain ATC currents as low as 0.02 and as high as 0.40 μ amp per sq cm. It is more probable that the observed effect of alloy weight on ATC current, Figure 5, is due to a combination of the barrier effect and an alteration of the steel base—alloy interface.

ATC Test in Other Media

The success of the ATC test in predicting corrosion performance in grapefruit juice and the relative ease which it can be conducted as compared with pack tests have led to a consideration of the possibility of using the same technique to determine corrosion performance in other media. In a preliminary investigation to pursue this possibility, 10 different samples of plate with a range of corrosion performance in grapefruit juice from good to poor were selected for testing in various media.

Table 12 summarizes the results of

TABLE 9—Effect of Exposed Steel Base on ATC Current

Area of Steel Exposed, Percent	ATC Current, μ amp/sq cm	
	Observed	Calculated
Small Areas:*		
0.0	0.09	....
0.2	0.10	0.09
0.4	0.10	0.09
0.9	0.10	0.10
1.8	0.10	0.10
Large Areas:*		
25	0.32	0.33
50	0.66	0.55
75	0.78	0.77
100	1.00	....

* Small areas were exposed by scratching lines approximately 0.0032 cm wide and 2.54 cm long on the sample.
** Large areas were detinned in a solution of SbCl₃ in concentrated HCl.

TABLE 10—Effect of Deforming the Tin Plate on the ATC Current

Sample	ATC Current, μ amp/sq cm	
	Deformed	Normal
A-9	0.20	0.20
B-9	0.05	0.07
C-9	0.24	0.26
D-9	0.12	0.09
E-9	0.21	0.27
F-9	0.09	0.10
Average*	0.15	0.16
I-9	0.51	0.60
J-9	0.07	0.06
K-9	0.57	0.52
L-9	0.32	0.32
Average**	0.38	0.37

* Deformed samples A to F were cut from cans.
** Deformed samples I to L were bent over a ¾-inch mandrel.

TABLE 11—Effect of Alloy Weight on ATC Current

Lot No.	Alloy Weight,* lb. Sn/bb	ATC Current, μ amp/sq cm
AL-1	0.00	1.05
AL-2	0.029	0.30
AL-3	0.052	0.26
AL-4	0.100	0.16
AL-5	0.116	0.10
AL-6	0.118	0.08
AM-1	0.00	1.10
AM-2	0.036	0.37
AM-3	0.103	0.20
AM-4	0.106	0.09
AM-5	0.128	0.08
AF-1	0.00	1.35
AF-2	0.032	0.52
AF-3	0.055	0.42
AF-4	0.115	0.38
AF-5	0.120	0.26
BV-1	0.00	0.81
BV-2	0.038	0.30
BV-3	0.068	0.22
BV-4	0.099	0.10
BV-5	0.103	0.08
C-1	0.00	1.20
C-2	0.018	0.57
C-3	0.059	0.37
C-4	0.091	0.12

* Specimens with zero alloy weight were prepared from matte plate.

these tests over a 3-day period and at three different temperatures. In general, increasing the temperature increases the ATC current in all media. Usually, the effect of temperature on a rate is shown as an Arrhenius plot of log k vs 1/T where k is a reaction-rate constant and T is the absolute temperature. Figure 6 shows such a plot for the average ATC current per temperature setting for four corrosion media. (For this plot, the ATC current is assumed to be approximately proportional to a corrosion rate.) With the exception of prunes, the curves seem to have the same general slope. Average activation energies for grapefruit, pineapple, and tomato juice were calculated to be 11, 12, and 14 kilocalories, respectively. These values are introduced for comparison purposes only, and because of the nonlinearity of the curves, have doubtful significance.

In grapefruit, tomato, and pineapple juice, the 10 lots all rank in the same order, but the results in prune juice seem to be quite different, a finding that is consistent with a reported difference in corrosion mechanism.[3]

Although the ATC currents in tomato juice are somewhat lower than in grapefruit and pineapple juice, the differences are rather small compared with the known differences in pack life, tomato juice having a considerably longer pack life than that of grapefruit or pineapple juice. In this regard, it should be noted that in grapefruit juice 20 to 120 sq cm of exposed alloy per can would be necessary for pack-life values calculated from

ATC currents to agree with observed pack performance.

Summary

The ATC test correlates well with actual pack performance. The ATC current is decreased (improved) by increasing the FeSn₂ alloy weight. If it is assumed that the alloy has porosities ranging up to 30 percent, the ATC current and the effect of alloy weight can be explained by a simple masking of the steel base by the alloy. ATC tests performed in pineapple juice and in tomato juice rank materials in the same order as tests performed in grapefruit juice. Prune juice, however, does not rank various lots in the same order as the other juices; this behavior is consistent with a different corrosion mechanism prevailing in prune juice, as has previously been reported.

Still to be explained are (1) the surprising lack of improvement in grapefruit-juice pack performance with decreasing ATC current obtained by increasing the alloy weight, (2) the difficulty of calculating actual grapefruit-juice pack life from the observed ATC values and from a reasonable estimate of exposed alloy areas, and (3) the relatively small differences in ATC currents obtained in various media for a given lot of tin plate, although the pack-life values are quite different in these media.

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TABLE 12—ATC Current in Various Fruit Juices and at Various Temperatures

	Average* ATC Current, μ amp/sq cm											
	Grapefruit			Tomato			Pineapple			Prune		
Sample	20 C	30 C	40 C	20 C	30 C	40 C	20 C	30 C	40 C	20 C	30 C	40 C
1	0.01	0.02	0.07	0.01	0.02	0.09	0.02	0.02	0.08	0.14	0.17	0.65
2	0.02	0.03	0.07	0.02	0.03	0.09	0.02	0.03	0.09	0.13	0.14	0.69
3	0.05	0.08	0.18	0.03	0.06	0.18	0.03	0.04	0.14	0.14	0.19	0.79
4	0.06	0.11	0.25	0.05	0.08	0.17	0.06	0.09	0.25	0.25	0.24	1.10
5	0.08	0.13	0.27	0.06	0.09	0.19	0.05	0.11	0.27	0.20	0.21	0.84
6	0.12	0.19	0.28	0.06	0.10	0.22	0.08	0.15	0.30	0.16	0.18	0.99
7	0.11	0.16	0.37	0.06	0.11	0.31	0.06	0.14	0.33	0.21	0.26	0.91
8	0.14	0.16	0.37	0.07	0.11	0.38	0.09	0.16	0.38	0.23	0.26	0.99
9	0.23	0.35	0.64	0.13	0.19	0.46	0.17	0.28	0.52	0.20	0.22	0.51
10	0.24	0.28	0.85	0.13	0.14	0.45	0.18	0.23	0.61	0.23	0.26	0.90
Avg	0.10	0.15	0.33	0.06	0.10	0.28	0.08	0.13	0.29	0.19	0.21	0.84

* Values were averaged over a 3-day period.

Corrosion Resistance of Electrolytic Tin Plate*

By G. G. KAMM and A. R. WILLEY*

Introduction

SINCE THE discovery by Kohman and Sanborn[1] and by Lueck and Blair[2] that tin offers electrochemical protection to steel in the air-free systems that are present in most food containers, a great many investigators have done work on the mechanism of tin plate corrosion. Studies reported by Culpepper and Moon,[3] Hoar,[4] and Morris and Bryan[5,6] contributed to a better understanding of the factors involved. Many other workers reported findings relating to performance of tin plate in a wide variety of food products. A thorough review of the literature on this subject through the year 1949 was made by Hartwell.[7]

As a result of the early researches it is well known that the corrosion of steel is inhibited by the presence of soluble stannous tin and that steel is protected cathodically when coupled to tin in many air-free acid media. More recent investigations reported by Vaurio,[8] Koehler,[9] Willey, Krickl, and Hartwell,[10] and Koehler and Canonico[11] have dealt with the mechanism of corrosion in plain tin plate[(1)] cans for acid foods. These studies provided information concerning potential and couple current relationships for tin and steel in typical products and test media, which findings all added to the general understanding of container corrosion. However, there has remained a need for additional test methods capable of measuring factors important to plate quality which were not measured by existing tests.

The information reported in this paper

Abstract

Several types of failure observed in tin plate containers are described in terms of tin-steel potential and current relationships. The effect of Sn++ on potentials and polarization of tin and steel electrodes in deaerated 1N HCl and 0.1M citrate buffer is shown to be important to proper design of electrochemical test methods. Potential and polarization measurements indicate that inhibition by Sn++ is not a plating-out process. Hydrogen diffusion experiments suggest a relationship between hydrogen diffusion and inhibition by Sn++. Polarization studies have identified the iron-tin alloy as an important factor in tin plate corrosion.
3.8.2, 6.3.14, 3.6.8

is the result of investigations undertaken to establish the electrochemical relationships of tin and steel in air-free acid media and the effect of soluble stannous tin on these relationships. The ultimate object was to develop new means for determining factors responsible for variations in corrosion resistance of electrolytic tin plate in plain cans for moderately acid foods, such as grapefruit juice and similar products.

Review of Theory

Before defining the specific area of container corrosion to be covered, it is necessary first to review the principles involved and the type of corrosion observed in plain tin plate containers. In order for tin plate to serve most effectively as a container material two conditions must be met: (a) tin must be sufficiently anodic to steel to provide complete cathodic protection of any steel exposed through pores or voids in the tin and iron-tin alloy, and (b) the rate of dissolution of tin must be slow enough

that the container will not fail early due to rapid hydrogen formation at the cathodic steel surface.

The Steel Electrode

It has been shown by other investigators[12,13,14] that the single electrode potential of any corrodible metal is not that of the true reversible electrode, but is a potential determined by the individual potentials of the local anodes and cathodes and their polarization characteristics. This situation for a corroding steel electrode is represented schematically in Figure 1. The steel potential E_s is the result of polarization of the local anodes and cathodes from their original potentials E_a and E_c, respectively, by the corrosion current i_c. These relationships are dependent upon the composition of the steel and the nature of the corroding medium.

Application of an external source of cathodic current, such as would be supplied by coupling with tin, polarizes the steel to a more negative potential and reduces the amount of current flowing from the local anodes. For example, couple current I_1 polarizes the steel to potential E_1 and reduces the local action current to i_1, while an applied current of I_2 polarizes the entire surface to a potential equal to that of the local anodes, cutting the corrosion current on the steel surface to zero. According to the theory of cathodic protection advanced by Hoar[12] and Mears and Brown,[13] the current I_2 required for complete protection must be equal to or greater than the initial local

(1) The term "plain" is used to designate cans which bear no internal organic lacquer or enamel coating or, in some instances, cans with plain bodies and enameled ends.
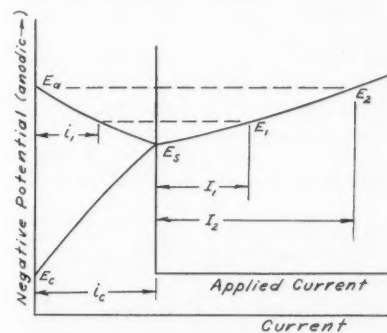
Figure 1—Schematic diagram showing potentials and polarization of the local anodes, E_a, and cathodes, E_c, of a corroding steel electrode, and the effect of an applied cathodic current, I, in reducing local action corrosion, i_c.

a. Normal Performance

b. Rapid Detinning

c. Partial Detinning — Pitting

d. Pitting — No Detinning
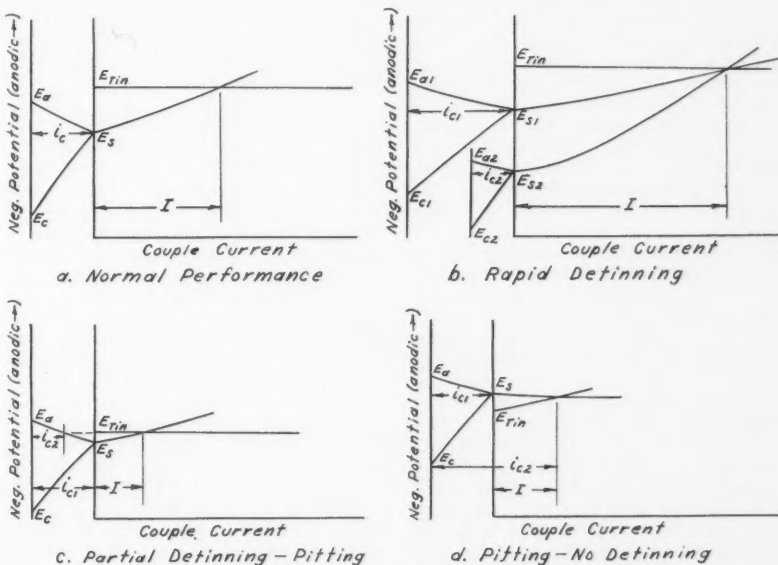
Figure 2—Schematic diagrams representing types of galvanic corrosion observed in tin plate containers.
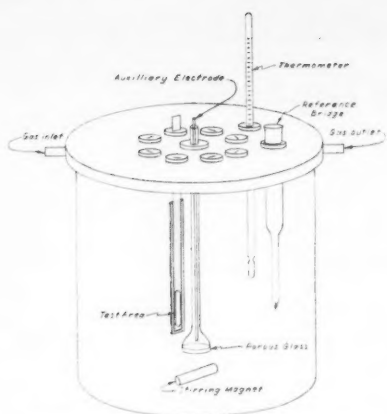
Figure 3—Test cell used in potential and polarization studies.

Figure 4—Polarization of tin and steel in deaerated 1N HCl containing no added Sn++.

action current i_c. Application of current in excess of I_2 will be wasted since no further protection can be achieved.

The Tin Electrode

In the media considered in this investigation, tin is observed to be anodic to steel, and corrodes at a low rate when uncoupled. The high negative potential is attributed to the complexing effect of ions such as citrate, chloride, hydroxyl and others[1,4,15] which reduce the concentration of Sn^{++} to extremely low levels, and to the high hydrogen overvoltage[2] which permits easy polarization of local cathodic areas with negligible corrosion currents. The tin electrode is less easily polarized anodically, and because of the extremely large area of tin anode as compared to the area of exposed steel cathode to be protected in a tin plate container, the tin may be considered as unpolarized by the low anodic current densities involved.

Types of Failure in Plain Tin Plate Cans

In the tin plate container, failure will result from either swells or springers[2] due to hydrogen formed by the corrosion processes, or from perforation of the can wall. The hydrogen can be formed by two distinct processes: (a) hydrogen formed at the exposed steel areas which are protected cathodically by the tin-steel couple current, and (b) hydrogen formed as the steel corrodes, either because it is not completely protected by tin or after the tin has been consumed.

_____
[2] Canned foods become unmerchantable when the can ends bulge outward or swell from internal pressure.

The diagrams in Figure 2 which will be discussed below are schematic representations of tin-steel potential relationships believed to obtain in tin plate cans under steady state conditions. They are based on information from test packs, including rates of tin and iron corrosion and visual observation of corrosion patterns.

a. **Normal performance.** The ideal situation, and that which appears to be approached in many of the moderately acid foods, is that represented in Figure 2a. In this instance the steel is completely protected by the cathodic current supplied by coupling with tin, and the couple current is only slightly greater than that required for complete cathodic protection of the steel. The nature and amount of exposed steel are such that the rate of tin dissolution, causing formation of cathodic hydrogen at the steel surface, is low enough to afford adequate shelf life, with failure occurring only after nearly all of the tin is gone from the container walls.

b. **Early failures due to tin-steel couple action.** There are similar situations in which the galvanic couple current flowing between the tin and steel is again sufficient to protect the steel from corrosion by local action, but because of potential and polarization relationships the tin-steel couple current is much

greater than normal. This results in rapid dissolution of the tin coating and early failures as hydrogen swells. As depicted in Figure 2b, this could conceivably be due to a fast corroding steel having a potential E_{s1} relatively close to the potential of tin, or to a slower corroding steel having a more cathodic corrosion potential E_{s2}. The amount of steel exposed is also an important factor in determining the rate of detinning in this case.

c. **Early failure by partial detinning and pitting.** There are instances of early failures (Figure 2c) in which the can is only partially detinned and pitting of the base steel is apparent. Here the tin is still anodic to the corrosion potential of steel E_s, but is slightly cathodic to the potential of the most anodic steel areas E_{s1}. The potentials of tin and steel would indicate that tin should provide protection; the couple current would seem to verify this. However, because of the relative potentials shown in the diagram, the couple current I provides only partial protection to exposed steel, reducing the local action corrosion at the steel surface to i_{c2}. Vacuum loss in the can occurs as a result of hydrogen generated by both the tin-steel couple current and the local action corrosion current at the steel surface. Failure usually occurs as a hydrogen swell although perforations are sometimes encountered.

TABLE 1—Hydrogen Diffusion Data

Period, Hrs.	CURRENT		Anode	Evolved H_2, ml/hr	Diffused H_2, ml/hr	Total H_2, ml/hr	Steel Potential, mv.
	μ amp	H_2 Equiv, ml/hr					
0.	uncoupled			.....	.....	.....	−687
0— 3.	2,000	0.84	Pt	1.06	0.02	1.08	−690
3— 6.	2,000	0.84	Sn	0.67	0.06	0.73	−737
6—11.	1,000	0.42	"	0.32	0.11	0.43	−745
11—22.	850	0.36	"	0.25	0.13	0.38	−740
22—31.	uncoupled			(final) 0.80	0.025	0.83	−640
31—47.	1,000	0.42	"	0.31	0.14	0.45	−740
47—50.	uncoupled			0.46	0.031	0.49	−655

d. **Early failure by pitting with no de-tinning.** The third type of early failure to be considered is the case of reversed tin and steel potential relationships in which the corrosion potential of tin is cathodic to that of steel as shown in Figure 2d. In this situation the tin-steel couple current I actually adds to the normal steel corrosion current i_{c1} causing accelerated pitting corrosion equivalent to i_{c2} at exposed steel areas. The high hydrogen overvoltage of the cathodic tin surface tends to minimize this accelerating effect, but because of the extremely large tin to steel area ratio the reversed couple current speeds the pitting process to some extent. Failure is by hydrogen swells or perforations.

There are some products containing depolarizers, or oxidants, which attack tin directly. This direct corrosion of tin produces no hydrogen, but added to the corrosion by the above mechanisms shortens the life of the tin plate container.

Experience with test packs of various food products which are relatively free of depolarizers has indicated that corrosion ordinarily takes place by the mechanism described under "a" and "b" above. Failure is by hydrogen swells with negligible iron in solution until after the tin has been consumed by the corrosion process, indicating that the steel is protected cathodically by the tin-steel couple current. Furthermore, the rate at which tin goes into solution is controlled almost entirely by the galvanic couple action. This class of products is typified by grapefruit juice and includes, among others, orange juice, tomato juice, tomatoes, peaches, pears, and pineapple products. Evidence has been cited by Frankenthal, Carter, and Laubscher[16] which indicated that depolarizers are present in prunes but appeared to be absent in grapefruit juice and tomato juice. Koehler and Canonico[11] have discussed the relative absence of depolarizers in peaches.

The type of corrosion described under "c" above has been observed mainly in cases of abnormal food product or inferior base steel properties for a particular application, either of which can affect the tin-steel potential relationships. Test packs at the authors' laboratories in which prunes were packed in tin plate made from high pickle lag steel[10, 17] have shown this type of failure; Koehler[9] and Koehler and Canonico[11] have described tin-steel couple studies with high pickle lag steel in which only partial protection of the steel was evident. Similar corrosion was reported by Vaurio, Clark, and Lueck[18] in early work with high silicon and high phosphorus steels. Cases of abnormal product corrosivity have also been observed to cause this type of failure with steels which give satisfactory performance with normal product.

Most products which in plain cans cause corrosion of the pitting type described in "d" above, are packed in fully enameled cans. Early failure by pitting corrosion in plain cans is, in most cases, the result of an abnormal product or base steel.

A more detailed discussion of relative performance of various tin plates in a number of food products will be presented in a later paper in this series.

From the above discussion it follows that in designing electrochemical tests for evaluating corrosion resistance of tin plate in a given product, the type of corrosion involved must be considered in order to determine what measurements should be made and to establish their significance. Similarly, in studies of product corrosivity, potential and current measurements will indicate the type of corrosion to be expected. Such measurements can be helpful in determining corrosivity of new products and in recognizing abnormal corrosivity of known products.

Figure 5—Effect of added Sn++ on potentials and polarization of tin and steel in deaerated 1N HCl.
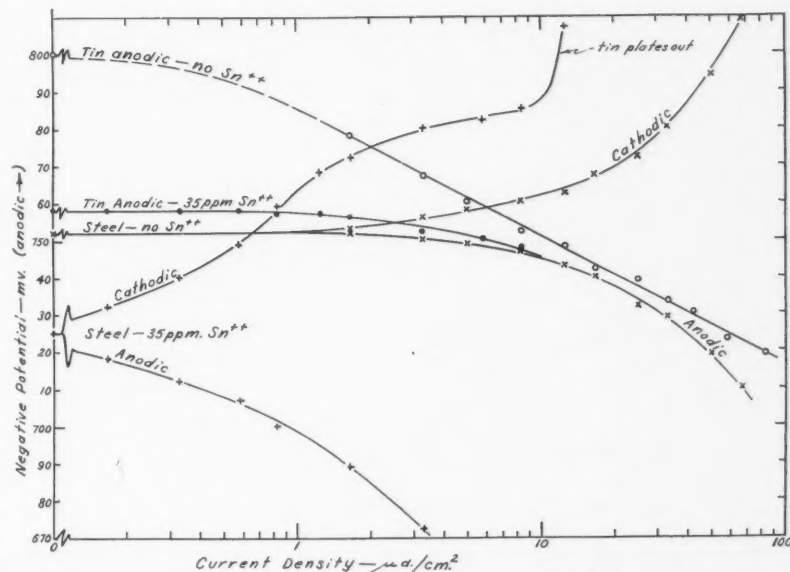
Figure 6—Effect of added Sn++ on potentials and polarization of tin and steel in deaerated 0.1M citrate buffer, pH 3.8.

Experimental and Discussion

Effect of Sn++ on Electrochemical Characteristics of Tin and Steel

Experiments were conducted to establish the tin and steel potential relationships in air-free acid media. The object was to determine the effect of soluble stannous tin on the potentials and polarization characteristics of tin and steel electrodes and to relate these findings to corrosion conditions present in tin plate containers packed with typical food products. Early experiments consisted of potential and polarization studies of tin and steel electrodes in deaerated 1N HCl and 0.1M citrate buffer (pH 3.8), with and without added Sn++. These were

Figure 7—Effect of added Sn⁺⁺ on the potentials of uncoupled tin and steel, and the potential of equal areas of tin and steel coupled, all in the same 0.1M citrate buffer solution, pH 3.8.

Figure 8—Potential decay curve for a steel electrode on which a small amount of tin had been plated (in 0.1M citrate buffer, pH 3.8 containing 35 ppm Sn⁺⁺).

Figure 9—Apparatus employed in hydrogen diffusion studies.

The solutions used were deaerated by heating to boiling; the boiling solution was poured into the cell, the top was put in place, and the headspace flushed with oxygen-free hydrogen or nitrogen. To maintain deaerated conditions the gas flow was continued at a low rate except when a sample was inserted or removed from the cell, at which time the flow was increased to prevent entrance of air while the stopper was removed. All tests were conducted at room temperature which ranged from 25 to 26 C.

Tin and steel electrodes were cathodically cleaned in room temperature 0.5 percent Na_2CO_3 solution at 10 volts, using a stainless steel or carbon anode, until no water break was apparent. They were then rinsed with deionized water, and dried with acetone prior to masking with microcrystalline wax (140 F melting point) to expose a known test area.

In all polarization experiments the sample was placed in the test cell and the potential was followed until it reached a relatively steady value and changed no more than 0.5 mv per minute. The polarizing current was then applied and the potential measured after 30 seconds at each current level.

b. **Studies in 1N HCl.** The anodic and cathodic polarization of a high purity tin electrode in 1N HCl with no added Sn⁺⁺ is shown in Figure 4. It may be seen that tin polarizes very steeply cathodically, behaving as a hydrogen electrode. The corrosion current determined by the method of Stern[19] is 0.20 μa./cm.², indicating a very low rate of corrosion in this medium.

The tin is more difficult to polarize anodically. As will be shown later in discussion of Figures 5, 6, and 7, the tin behaves as a Sn/Sn⁺⁺ electrode, and concentration of Sn⁺⁺ in the test solution affects the anodic polarization.

Data for a Type L steel[3] electrode also appear in Figure 4. The indicated corrosion current of 250 μamp/cm² is approximately 1,000 times that observed for tin in the same solution. High current densities are required for appreciable polarization.

[3] "Type L" designates a steel of low metalloid, low residual metal content employed in the container industry.

chosen as typical media in which tin is anodic to steel.

a. **Apparatus and procedure.** The type of cell used for polarization experiments is illustrated by Figure 3. A 900 ml borosilicate vessel was fitted with a plastic top in which holes and passages were machined to (1) permit sweeping of the headspace with a suitable gas, and (2) provide means for inserting samples, a platinum auxiliary electrode, and a reference probe. The top was sealed to the cell by means of a polychloroprene "O" ring which had been treated in boiling 10 percent NaOH for 5 minutes to remove traces of sulfur from the rubber.

Silicone rubber grommets and slitted stoppers were used to effect a seal around the samples and other items inserted in the cell. The auxiliary electrode compartment consisted of a tube with a porous glass disc at the end to allow flow of current with minimum diffusion of oxygen into the main test solution.

A 90 volt battery connected in series with suitable variable resistors was used as a source of polarizing current, the current being measured as the potential drop across a precision resistor. A Beckman Model G pH meter was used to measure potentials with respect to a 0.1N calomel reference electrode.

Figure 10—Hydrogen evolved from and diffused through a 5 cm² disc of Type L steel (0.0094 inch thick) coupled to tin in deaerated 3N HCl.

Figure 11—Potential shift of a steel electrode upon uncoupling after being coupled to tin in deaerated 1N HCl containing 40 ppm Sn++.

Figure 12—Cathodic polarization of the alloy surface of tin plates in deaerated 1N HCl (no added Sn++).

Additional studies were conducted with the same samples after adding 40 ppm of Sn++ as $SnCl_2 \cdot 2H_2O$ to the test solution. The resulting polarization curves are plotted in Figure 5, along with data obtained with no Sn++ added. The potential of the tin electrode has been displaced by 41 mv in the positive direction. Very little anodic polarization is observed for current densities below 60 $\mu amp/cm^2$. Only at anodic current densities above 100 $\mu amp/cm^2$ does the curve approach that obtained with no added Sn++. The potential of the steel electrode is relatively unchanged by the addition of Sn++, although by the time the anodic curve was measured the potential had shifted 11 mv in the positive direction. Both anodic and cathodic polarization are much more rapid than before. The local action current i_c cannot be determined in the presence of Sn++ since at potentials above the corrosion potential of tin in that solution, tin plates out on the steel surface which then behaves as a tin electrode, polarizing very steeply.

Taking the intersection of the anodic tin and cathodic steel polarization curves as a prediction of couple current, it is apparent that the addition of 40 ppm Sn++ reduces the couple current from 280 to 57 $\mu amp/cm^2$ and at the same time provides increased cathodic protection as evidenced by the 15 mv additional cathodic polarization of the steel electrode. When the tin and steel electrodes were coupled, the initial currents approached the values predicted from the polarization curves, but gradually drifted to lower values until steady state conditions were reached. This was to be expected because the polarization curves were not measured under steady state conditions and therefore would not predict the steady state couple currents.

c. Studies in 0.1M citrate buffer, pH 3.8. Polarization studies for pure tin and Type L steel electrodes in deaerated 0.1M citric acid buffered to pH 3.8 with sodium hydroxide were conducted in the manner described above, except for the method of introducing the Sn++. Tin was added to the cell by anodic dissolution
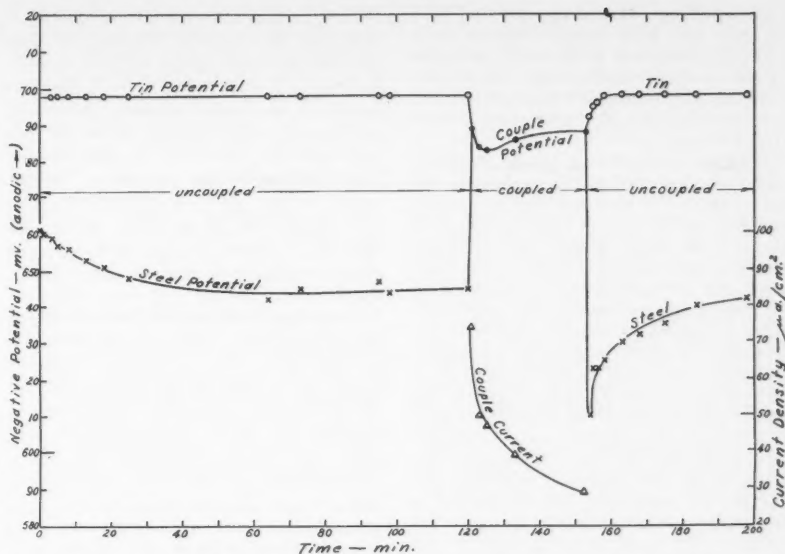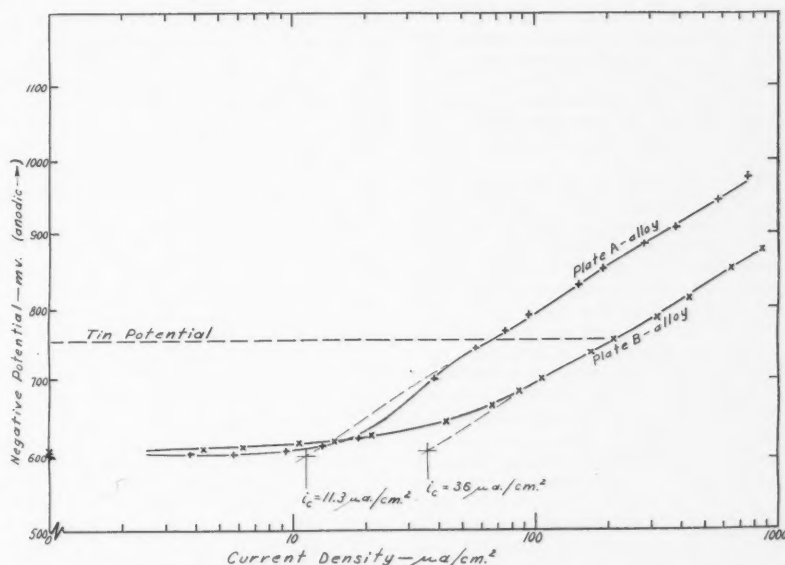
of a tin electrode, using the platinum electrode as cathode and measuring the current flow to give a rough measure of the amount added. The solution was later analyzed polarographically for tin content.

As seen in Figure 6, the slope of the anodic polarization curve of tin is slightly greater than that observed for anodic polarization of tin in the 1N HCl, probably because of limited diffusion of Sn++ from the electrode or of citrate ion which complexes much of the Sn++. Addition of 35 ppm of Sn++ shifts the tin potential and alters its polarization curve in much the same way as in the 1N HCl. Only at relatively high current densities is the tin polarized appreciably.

The corrosion potential of the steel

electrode moves in the positive direction by an amount slightly less than that observed for tin, and both anodic and cathodic polarization are increased markedly by the addition of the Sn++. Again, in the presence of Sn++, and at potentials anodic to the corrosion potential of tin, deposition of tin occurs at the cathodically polarized steel surface, causing it to polarize steeply as a tin electrode.

With no added Sn++ the intersection of the anodic tin and cathodic steel polarization curves indicates a couple current of 6.1 $\mu amp/cm^2$ and the steel is polarized cathodically by only 6 mv. Upon adding 35 ppm of Sn++ the indicated couple current is reduced to 0.83 $\mu amp/cm^2$, but the steel is polarized cathodi-

cally by 33 mv. Thus it appears that with no Sn++ the high current affords little cathodic protection to the steel; addition of Sn++ not only reduces the couple current but also establishes conditions more favorable to cathodic protection of the steel electrode.

d. **Effect of Sn++ on single electrode and couple potentials.** To determine the concentration of Sn++ required to provide cathodic protection of steel coupled to tin in 0.1M citrate buffer, pH 3.8, single electrode potentials of uncoupled tin and steel and the potential of equal areas of tin and steel, coupled in the same cell, were measured at various Sn++ concentrations. The Sn++ was added by anodic dissolution of a tin electrode. The data, plotted in Figure 7, show that the tin reacts to added Sn++ as a Sn/Sn++ electrode, while the potential of steel is also forced in the cathodic direction. The slope of the line is slightly less than that for the tin electrode. This is, indeed, a fortunate circumstance that the steel behaves in this manner, for it may be seen that at Sn++ concentrations greater than 27 ppm the potential of tin is cathodic to the initial steel potential.

It is also apparent from the potential of the couple as compared to the potentials of the uncoupled electrodes that little, if any, cathodic protection is afforded the steel by coupling to tin at 1 ppm Sn++. Concentrations of approximately 10 ppm or more are required for maximum cathodic polarization of the steel.

These observations in both 1N HCl and 0.1M citrate buffer emphasize the importance of having a large tin to steel area ratio in couple studies run in solutions containing no Sn++ initially, and explain the results reported by Kohman and Sanborn[1] on the effect of relative areas of tin and steel on the degree of protection obtained. For complete protection of the steel either a large tin to steel area ratio or the presence of more than 10 ppm of Sn++ is required. In most products packed in plain cans one or both of these conditions are met throughout the life of the container. The area of the tin surface in a can is very large with respect to the area of steel exposed. Shortly after processing the Sn++ concentration will exceed the minimum desirable.

Observations Pertaining to the Mechanism of Inhibition by Sn++

Although theories concerning inhibition by Sn++ have been offered in the past, the actual mechanism is not well understood. Certain experimental observations made in the laboratory, which, while not providing a definite answer, seem to have a bearing on this phenomenon.

It is generally accepted that for solutions in which tin is anodic to steel the inhibiting effect of Sn++ on the rate of steel corrosion is not the result of tin plating out on the steel surface. Further proof of this appears in Figure 8 which represents the potential decay curve for a steel electrode which was polarized cathodically in 0.1M citrate buffer containing 35 ppm Sn++ (Figure 6) until tin

started to plate out on its surface. It is seen that upon cutting the cathodic current the potential drops rapidly at first. It levels off at a value close to the potential of tin in that solution, then drifts slowly to a value slightly below the initial corrosion potential of steel, as the tin is dissolved from the surface by galvanic action. Thus the potential shift with deposition of metallic tin on the steel is opposite to that which results from addition of Sn++ to the solution (Figure 7).

Hoar and Havenhand[20] have attributed the shift of the steel potential observed on addition of Sn++ to anodic inhibition which presumably affects the polarization of local anodes on the steel surface. Observations to be described here suggest that the potential shift and corrosion inhibition are the result of hydrogen diffusing into the steel as an alloying substance which could conceivably alter the potentials and polarization of both local anodes and cathodes on its surface.

The diffusion of hydrogen through steel is well known. Morris and Bryan[6] found that the relative amounts evolved and diffused were affected by the quality of the steel and also by substances added to the corroding medium. Davis and Butler[21] have reported rapid diffusion of hydrogen through tin plate steels subjected to attack by acid media. The work reported below was undertaken in an attempt to determine the rate of hydrogen diffusion through Type L steel protected by a cathodic current.
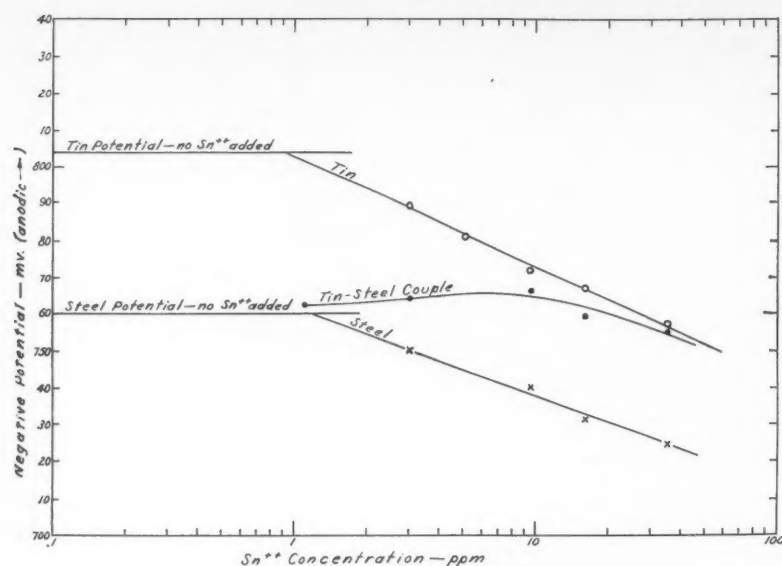
The experiments were conducted in the apparatus shown in Figure 9 which provided means for measuring evolved and diffused hydrogen, the cathodic current supplied to the steel sample, and the potential of the steel measured with respect to a 0.1N calomel reference. A disc of 0.0094 inch thick Type L steel (5 cm² exposed) was exposed to a deaerated 3N HCl solution on the top side, and to nitrogen under a slight vacuum, imposed by the column of dibutyl phthalate, on the opposite side. During most of the test the steel was coupled to a pure tin wire electrode (40 cm²).

To determine the effect of cathodic protection with no Sn++, a platinum wire anode was used during the first three hours of the test, and a battery and variable resistor were placed in the circuit to provide a cathodic current to the sample.

After three hours the platinum anode and the battery were removed and the tin anode inserted, coupled to the steel sample through a 1 ohm precision resistor to permit current measurements. The tin and steel remained coupled except for two short periods in which the steel was allowed to corrode freely. The rates of hydrogen diffusion and evolution are shown in ml/hr along the appropriate curves in Figure 10.

Table 1 lists the rates of diffusion and evolution, the average currents for the various time periods obtained by integrating the current-time curve, and the potentials for the tin-steel couple or uncoupled steel, as the case may be.

The following observations are considered important:

1. With no Sn++ present, high cathodic currents provided only partial protection of the steel and very little hydrogen diffused through the steel. The steel was polarized only 3 mv cathodically.

2. Sn++ added by anodic dissolution of the tin electrode caused the steel to polarize more easily cathodically and shifted its corrosion potential (uncoupled) in the positive direction.

3. With Sn++ present, during the periods 6 to 11 hours, 11 to 22 hours, and 31 to 47 hours when the steel was coupled to tin, the rate of diffusion was markedly greater and the total hydrogen generated was approximately equivalent to the rate of anodic dissolution of the tin (calculated from the couple current). This indicated that the steel was essentially completely protected from corrosion.

4. The rate of hydrogen diffusion with the steel coupled to tin was approximately 4 times the rate uncoupled, and amounted to ⅓ of the total generated.

5. The total corrosion observed for the tin-steel couple as evidenced by measured hydrogen was little more than half that measured for the uncoupled steel alone.

The decrease in total corrosion upon coupling of steel to tin indicates that the steel was protected by a cathodic current which was less than the local action corrosion current of the uncoupled steel in the same Sn++ containing solution. This is contrary to the accepted theory of cathodic protection[12,13] unless a change occurs in either the nature of the surface or its environment. Evidence of decreased total corrosion upon coupling steel to tin may be found in reports by early investigators[1,2,6] but is not clear cut because of uncontrolled Sn++ concentration. Koehler[9] recognized this phenomenon under controlled conditions and related it to a shift in potential of the steel electrode. He reported that upon uncoupling a steel sample which has been coupled to tin for 24 hours, the potential of the steel shifts rapidly in the positive direction for less than one minute after which it shifts slowly in the negative direction.

Evidence of such a potential shift is shown in Figure 11 which represents potential measurements for equal areas of tin and steel, both coupled and uncoupled, in 1N HCl containing 40 ppm of Sn++. Upon uncoupling, the potential of the steel drops to a value 35 mv cathodic to the initial corrosion potential and then gradually drifts back in the negative direction, leveling off at a value close to the former uncoupled potential. It appears that when steel is coupled to tin in the presence of Sn++ the potential of the steel actually becomes more noble and also becomes more easily polarized cathodically as evidenced by decreasing couple current with time, also shown in Figure 11.

The significance of the data presented here lies in the possible connection between diffusion of hydrogen into the steel in the presence of Sn++ and the unexplained inhibiting effect of Sn++ and coupling with tin. It may be postulated

that the potential shift in the positive direction and change in polarization of the steel is caused by hydrogen entering the steel lattice; it is conceivable that the shift in potential of freely corroding steel upon addition of Sn^{++} is also a result of a change in the amount of hydrogen diffusing into the steel. Application of a protective cathodic current further increases the diffusion with an additional shift in the positive direction. A similar shift in potential, accompanied by increased polarization, was observed for steel polarized cathodically with no Sn^{++} present, but the effect is less even at much higher current densities. The drift toward the original corrosion potential after uncoupling indicates the time required for hydrogen to diffuse out of the steel surface to re-establish the original steady state conditions. Further work will be required to evaluate this hypothesis.

The rapid diffusion of hydrogen when the steel is coupled to tin may also account for the fact that in a product such as grapefruit juice, which contains no depolarizers, and with plate which gives extremely good pack performance, the rate of vacuum loss is less than would be expected from the rate of dissolution of tin. In this case where the rate of hydrogen generation is extremely low, much of it may diffuse into or out through the can walls. This accounts for the fact that only part of the original vacuum is lost during the detinning phase of the corrosion process and rapid failure as a hydrogen swell occurs only when tin has been consumed and the unprotected steel base begins to corrode.

Although hydrogen does not diffuse through a continuous film of tin, diffusion experiments in which the tin coating was not removed from the side of the plate opposite to that exposed to the corroding medium have shown that hydrogen can diffuse out through pores in the tin coating. This has been observed both visually and by measuring the amount diffused.

Identification of Factors Related to Corrosion Resistance

In view of the variations observed in the corrosion resistance of present day electrolytic tin plate,[7, 10, 22] research was undertaken to apply electrochemical techniques to the identification of factors responsible for these variations, with the hope of establishing improved test methods for controlling plate quality.

Techniques similar to those discussed earlier in this paper were employed to investigate the electrochemical characteristics of several plates of known good and poor quality. The plates used were electrolytic tin plates, made from Type L or MR steel,[(4)] which had been retained from lots of plate used in test packs of food products during the years previous, thus providing a record of their corrosion performance. Samples were available representing as much as a two-fold difference in service life in grapefruit juice and tomato juice test packs.

Because of evidence that the steel surface properties can play an important role in corrosion resistance,[10] efforts were directed to evaluation of the base steel and the iron-tin alloy which is composed partially of material from the original steel surface.

a. **Sample preparation.** One of the first problems was that of selecting methods of sample preparation which would expose alloy or steel surfaces without attacking them. Earlier work by Kunze and Willey[23] had shown that of the methods available for stripping to the alloy, only the electrolytic methods in NaOH[24, 25] were suitable for exposing the alloy without attacking it appreciably. Thus all samples tested at the alloy surface were cathodically cleaned in room temperature 0.5 percent Na_2CO_3 at 10 volts, then detinned electrolytically in room temperature 5 percent NaOH. For tests conducted at the steel surface the alloy was removed by treatment in hot (90 C) 10 percent NaOH solution to which small amounts of Na_2O_2 or H_2O_2 were added.

Samples so prepared were masked with microcrystalline wax (140 F melting point) to cover the back and all edges, exposing 0.50 cm^2 on the side to be tested. Gaskets could not be used to define test areas because of excessive corrosion at the edge of the gasket.

b. **Polarization studies.** The polarization technique is not well suited to the study of tin plate alloy and steel surface properties since in part of the test the sample is subjected to corrosion which may change the nature of the test surface. In the corrosion of tin plate the alloy and steel are protected galvanically, and since the nature of the uncorroded alloy and steel affect the detinning rate it is important that corrosion of the test surface be prevented. A cathodic conditioning current may be applied to prevent corrosion before the actual polarization, but even then some corrosion occurs during the low current measurements, and none of the measurements approach steady state conditions. Reproducibility was found to be only fair. Because of these disadvantages the polarization technique was later discarded, but not before certain important information was obtained.

Two lots of electrolytic tin plate, both from the same heat of steel but processed in different ways, were selected for tests because of a 2 to 1 difference in pack performance which could not be detected by the usual laboratory tests for corrosion resistance.[10] Plate A lasted twice as long as Plate B in tomato juice test packs stored at 100 F. These plates were subjected to cathodic polarization tests in a manner similar to that described earlier in this paper. Both iron-tin alloy and base steel surfaces were tested.

Although reproducibility was not as good as desired, measurements in both 1N HCl and 0.1M citrate buffer, pH 3.8 (no added Sn^{++}), detected differences in polarization of the alloy surfaces which consistently indicated plate B to be the faster corroding and more difficult to

polarize cathodically. Typical data for 1N HCl are shown in Figure 12. The indicated corrosion currents, i_c, determined by the method of Stern,[19] exhibit a three-fold difference. Also, if the alloy surfaces of the two plates were coupled to tin as in a can, and if one considers the large tin surface in a can essentially unpolarized, a much larger couple current would result in the case of plate B as indicated. The differences observed in other such comparisons were not always as great as those illustrated but were consistently in the direction correlating with pack performance. Similar results were obtained with several other plates of known corrosion resistance. In tests conducted at the steel surfaces, no significant differences were observed for these plates.

These results seemed to indicate that the difference between these plates is in the nature of the iron-tin alloys and not in the base steel. This is not too surprising, however, when one considers that even if the original steel surface were responsible for variations in quality, that surface becomes a part of the iron-tin alloy when the tin is melted to provide a bright finish.

c. **Couple current measurements.** The differences in electrochemical properties measured at the alloy surfaces, first detected by polarization techniques, were later confirmed by couple current measurements. Couple tests have the advantage of providing protection to the sample throughout the test, and currents can be measured after steady state conditions have been established. The details of such a test developed from this work will be covered in Part 2 of this series of papers.[26]

Summary

The types of corrosion failures observed in plain tin plate cans have been described in terms of electrochemical relationships. The type of failure involved must be considered in designing electrochemical tests for measuring corrosion resistance of the plate or corrosivity of the product to be packed. To be meaningful, short-term laboratory tests should simulate conditions in the container as closely as possible.

The amount of Sn^{++} in solution was found to affect the tin-steel potential and polarization relationships which in turn determine the magnitude of the couple current and the degree of protection afforded the steel. Maximum protection of the steel in a tin plate container is assured by (a) the relatively large area of the tin surface with respect to the steel and (b) the presence of Sn^{++} in the contents of the container during most of its service life.

Evidence in the form of potential and polarization measurements confirms the theory that inhibition of corrosion by Sn^{++} is not the result of metallic tin plating out on the steel surface in the test media employed. Hydrogen diffusion data suggest that the inhibiting effect of coupling steel to tin is related to the diffusion of hydrogen into the steel, a

(4) "Type MR" designates tin plate steel of low metalloid content similar to Type L but less restrictive with regard to residual metals.

process which appears to be catalyzed by the presence of Sn++. The data also suggest that a part of the hydrogen formed cathodically at exposed steel areas by the tin-steel couple current will diffuse through the can wall, while nearly all hydrogen generated by corrosion of unprotected steel will be evolved at the corroding surface.

Electrochemical properties measured at the steel and iron-tin alloy surfaces by polarization and couple techniques indicate that the nature of the alloy is an important factor in determining the corrosion resistance of electrolytic tin plate.

Acknowledgment

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PART 2—The Alloy-Tin Couple Test—A New Research Tool

By G. G. KAMM, A. R. WILLEY, R. E. BEESE and J. L. KRICKL

Introduction

THE CORROSION resistance of electrolytic tin plate has been under continuous study ever since 1937 when this type of plate was first made. Through persistent efforts on the part of can manufacturer and tin plate producer alike, improvements in plate quality have made possible substantial reductions in the average tin coating weight used for containers[1,2] with no sacrifice in container performance. In the last six or seven years most of these tin savings may be attributed to use of heavily coated electrolytic tin plate for a wide range of products previously packed only in hot dipped plates.[1]

The gradual improvement of electrolytic tin plate to its present state of development has been treated elsewhere.[1,2,3] For this reason it will not be covered in detail here, although a few comments are necessary to give perspective. Such factors as steel composition, ingot practice, and those stages of steel processing which long ago were found to have important effects on corrosion resistance of hot dipped tin plate could not explain the variations noted in the first electrolytic plates. The only method then capable of detecting and measuring the large performance variations was a time-consuming test pack. Around 1944, it was discovered that steel surface properties played an important role. Out of this grew the "rate of pickling" (pickle lag) and "iron solution" tests[2] which identified two sets of these

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surface factors and measured their intensities. Much of the progress in improving plate quality since that time may be attributed to the use of these tests for rapid identification of manufacturing variables which affect performance. More recently, tin crystal size has also been recognized as reflecting certain base steel surface factors related to corrosion resistance.[1] The importance of these properties is such that it is now

Abstract

A new 20 hour electrochemical test which measures the current flowing between pure tin and tin plate detinned to the alloy layer, coupled in deaerated grapefruit juice, shows good correlation with rate of detinning in grapefruit juice test packs. The test detects variations in corrosion resistance not measurable with other known short-term tests. A theory of tin plate corrosion based on relative porosities of tin and alloy layers has evolved from this work, providing a better understanding of factors involved in tin plate corrosion. This alloy-tin couple (ATC) test serves as a valuable tool in tin plate research.   2.3.5, 6.3.14
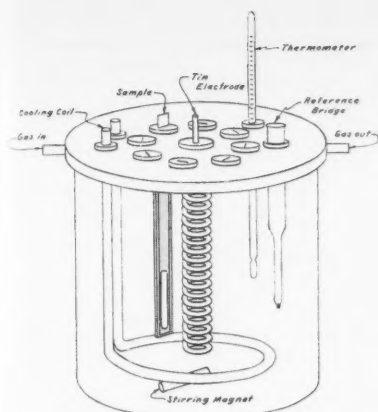
Figure 1—Test cell used in the ATC test.

TABLE 1—Effect of Deformation on ATC

| Plate | ATC-μ a./cm.² | |
	Unstrained	Deformed
A...............	0.024	0.084*
A...............	0.024	0.116**
U...............	0.34	0.34*
X...............	0.060	0.185*
Y...............	0.085	0.20**
Z...............	0.20	0.69*

* Entire surface strained approximately 12 percent in tensile tester.
** Major part of surface subjected to 180 degree bend of approximately 0.015 inch radius.

Figure 2—Schematic diagram of ATC test circuit.

common practice in commercial production of heavily coated electrolytic tin plate to aim for low pickle lag, low iron solution value (ISV) and large tin crystal size.[2] When plate has these desired characteristics, much of the earlier erratic behavior disappears. The resultant corrosion resistance is equivalent to, or greater than that obtained from common coke plate.

While all heavily coated electrolytic plates meeting pickle lag, ISV, and tin crystal size specifications give generally satisfactory performance, some of these plates exhibit superior corrosion resistance indicating that further improvement is possible. With some plates the steel is protected from corrosion much more efficiently by galvanic coupling with tin than is the case with the majority of plates tested. This is evident principally in plain cans[3] for a class of food products, which includes, among others, citrus products, tomato products, peaches, apples, and pineapple. This paper deals with the corrosion resistance of electrolytic tin plate for this class of products.

For convenience, the plate with superior corrosion resistance have been designated as Grade A and those with average corrosion resistance as Grade B. Pack tests with the so-called Grade B electrolytic tin plates (No. 100 or No. 100-25)

(2) Present commercial aims: pickle lag—10 sec. or less, ISV—20 micrograms of iron or less. tin crystal size—equal to or larger than ASTM non-ferrous grain size #9. (compared at 1X magnification)

(3) "Plain" refers to cans which bear no internal organic lacquer or enamel coatings or, in some instances, cans with plain bodies and enameled ends.

show that on the average it gives service life[4] equivalent to that of common coke (hot dipped) tin plate. The average service life for Grade A plates will be at least ⅓ greater than that of common coke plate.

For the purpose of this discussion, service life of No. 100 electrolytic plate in plain cans packed with grapefruit juice and stored at 100 F to accelerate corrosion will be used as a criterion of corrosion resistance. Grapefruit juice is used because it is typical of the class of food products mentioned above, and results with it may be applied validly to the class as a whole. Further evidence of this will appear in a later paper in this series.

The bulk of present day commercial production, which falls in the Grade B classification, exhibits service life in the range 14-22 months, and averaging about 18 months. A relatively small percentage of production qualifies as Grade A by consistently giving service life greater than 22 months, and in some cases more than 30 months. These service life figures are for 100 F storage and are considerably shorter than would be obtained in commercial packs which are normally stored at lower temperatures.

The differences in performance for Grades A and B cannot be accounted for on the basis of variation in base steel composition or microstructure, which are now closely controlled, nor can they be measured by the usual laboratory tests.

(4) The term "service life" is defined as the time required for 50 percent of the cans in a given lot to fail by formation of hydrogen springers.

Electrolytic plates having the desired pickle lag, ISV and tin crystal size, have been found to give Grade B performance or better, since these same properties are also important for Grade A. However pickle lag, ISV and tin crystal size, singly or together, do not distinguish between Grade A and Grade B. Without a good laboratory method for evaluating progress in improving plate toward the Grade A level, it was again necessary to resort to test packs as the sole means of evaluating attempted improvements in this area. Since plate of Grade A quality will last approximately two years or more in accelerated pack tests, at least one year was required before even rough indications of performance could be obtained and nearly two years elapsed before the final results were known. Rapid progress was virtually impossible.

As the result of work described in the first paper in this series,[4] a rapid electrochemical couple test was developed which detects factors important to Grade A performance which previously were measured only in test packs. This test, to be described below, has identified the iron-tin alloy layer as important in tin plate corrosion and has given new insight into the mechanism involved. The findings have been related to corrosion resistance of plain cans for the class of products typified by grapefruit juice in which corrosion is controlled by galvanic couple action. The test cannot be applied without further investigation to corrosion in fully enameled cans for corrosive fruits where the availability of tin is limited, or to corrosion by other products such as green beans or spinach
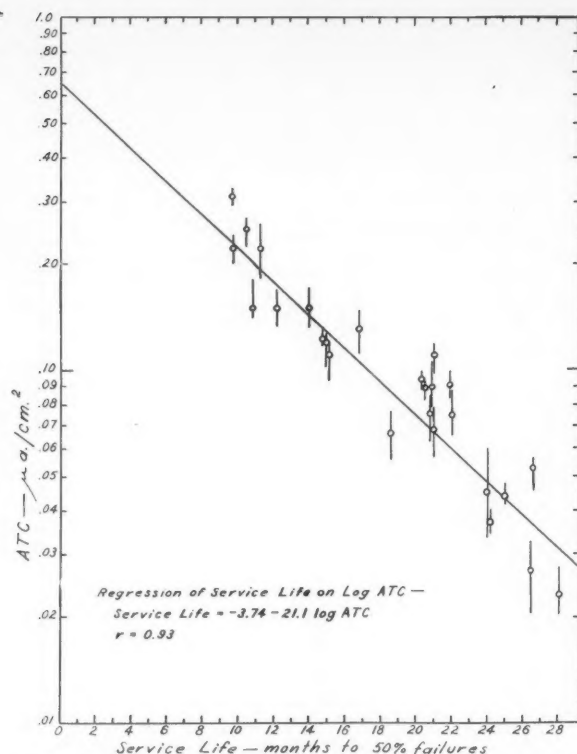
Figure 3—Relationship between log ATC and average performance in grapefruit juice pack stored at 100 F.
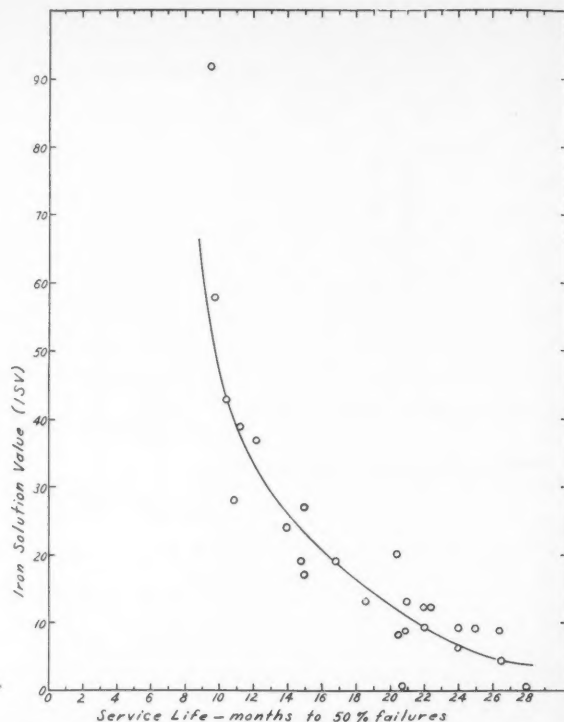
Figure 4—Relationship between ISV and average performance in grapefruit juice pack stored at 100 F.
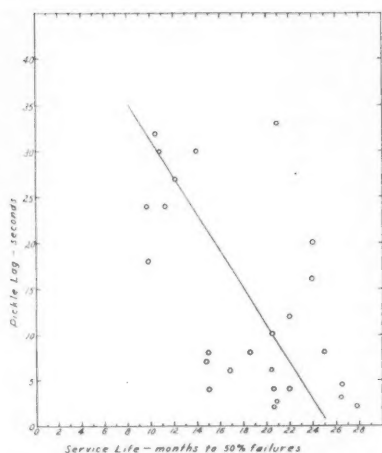
Figure 5—Relationship between pickle lag and average performance in grapefruit juice pack stored at 100 F.

in which direct attack of the tin is an important factor. Also, in the case of enameled cans for many vegetable, meat, and fish products the variations in tin plate corrosion resistance under consideration here do not show up and may be dismissed as unimportant.

The Alloy-Tin Couple Test

The alloy-tin couple test (ATC test) was designed to simulate closely the conditions existing in a tin plate container of grapefruit juice. Attention was given to the electrochemical factors important

to tin plate corrosion in this system in which steel was protected from corrosion by coupling with tin. The rate of detinning was determined by the galvanic couple current.

Briefly, the test consists of coupling the tin plate sample, which has been detinned to the alloy surface, to a pure tin electrode in deaerated grapefruit juice containing 100 ppm of soluble stannous tin. After 20 hours, the couple current flowing between the sample and the tin electrode is measured and expressed as current density in μ amp./cm.^{2} based on the area of the sample. This alloy-tin couple current density will be referred to as the ATC. Eight test samples are all coupled to a single pure tin electrode of relatively large area in a cell similar to that shown in Figure 1. Current measurements are made by inserting a low resistance galvanometer into the circuit as in Figure 2. A temperature of 79 F (26 C) has been adopted as standard test temperature.

To preserve continuity in this discussion details of test procedure are given in Appendix A. However, the following factors are mentioned briefly at this time as being important to the success of the test:

1. Use of a typical food product as test medium.

2. Oxygen-free conditions.

3. Controlled Sn^{++} concentration.

4. Sample preparation—method of detinning and masking.

5. Protection of the sample by coupling with tin throughout the test.

6. Size of tin electrode.

7. Controlled test temperature.

These factors are discussed in greater detail in Appendix B.

The correlation between ATC and pack performance has been established in two different ways. The first is that obtained by comparing ATC with an *average* performance in pack tests. Such a comparison is shown in Figure 3 as a semi-log plot of ATC vs service life in grapefruit juice packs at 100 F. The data represent 26 samples of No. 100 electrolytic plate which were produced to demonstrate the effect of tin mill processing variables on corrosion resistance. Each point represents service life data from a pack size of approximately nine cans and the average of at least four ATC determinations. The vertical line indicates the spread for the individual ATC values. The regression of service life on log ATC, calculated by the method of least squares from the individual ATC data and average service life, is expressed by the equation:

$$\text{Service Life} = -3.74 - 21.1 \log \text{ATC} \tag{1}$$

which describes the straight line shown in Figure 3. The correlation coefficient in this case is 0.93.

It is significant that the data show good correlation throughout the service life range represented, indicating that the ATC is capable of measuring differences in performance in the Grade A range. The ISV-service life plot for the same plates (Figure 4) shows good correlation below the 18 month performance
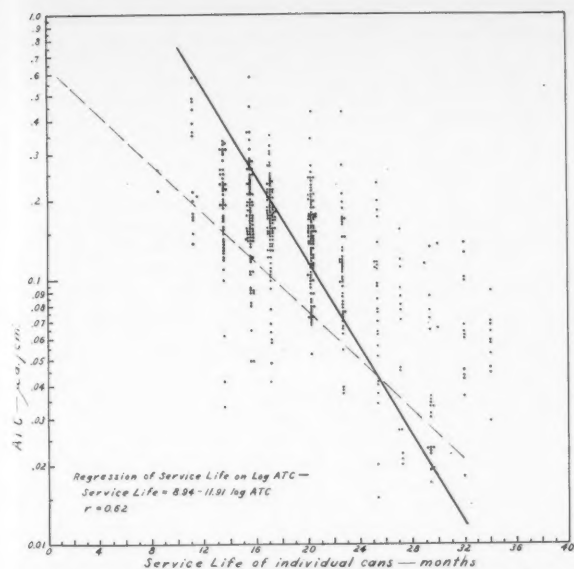
Figure 6—Relationship between single ATC data and performance of individual cans in grapefruit juice pack stored at 100 F. Plates tested represent tin mill line samples from thirteen producers.

Figure 7—Schematic representation of tin plate surface cross sections depicting relative porosities of the tin and alloy layers of Grade A and B plates.
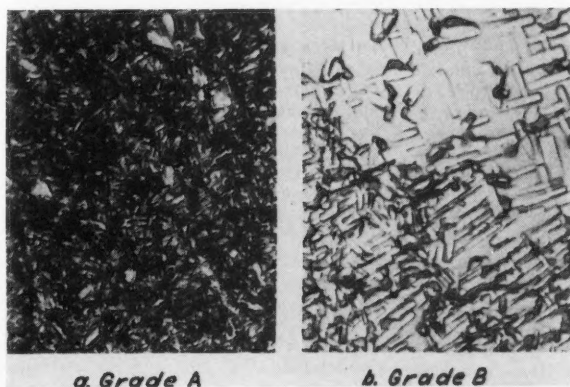
Figure 8—Typical alloy surfaces of tin plates with free tin removed electrolytically in NaOH, showing differences in alloy continuity and crystalline structure. (Electron micrographs of chromium shadowed carbon replicas—6500X magnification)

Figure 9—Corrosion of tin and steel in grapefruit juice pack stored at 100 F. Data obtained from analyses of tin and iron in the product at various storage intervals.

level but indicates a lack of sensitivity in the higher range of service life. Pickle lag (Figure 5) also shows a trend indicating a relationship to corrosion resistance. It is apparent that the ATC test measures factors related to pack performance for plates falling in the 18 to 30 month range which were not detected by ISV or pickle lag.

The significance of ATC was also put to a more severe test as shown in Figure 6. The data represent performance of individual cans plotted against the ATC obtained from plate adjacent to that used in making the can. More than 450 such comparisons are plotted which were obtained from single sheets of plate taken periodically as commercial line samples at fourteen different tin mills. These included the usual variations in tin coating weight, pickle lag, ISV, tin crystal size, and base steel composition and microstructure found in commercial production. Also, no attempt was made

to minimize the effect of can manufacturing or packing variables on service life by using an average pack performance. The regression of service life on log ATC is in this case:

Service Life = 8.94 — 11.91 log ATC (2)

which is shown as a solid line. This line provides for these data the best estimate of service life for plate of a given ATC. The correlation coefficient of 0.62 is extremely good considering the limited control of other variables. This indicates that of all variation in service life, including that due to plate, packing, and can manufacturing variables, 36 percent was accounted for by ATC alone. The regression line for the data in Figure 3 is shown as a broken line for comparison, indicating a difference in slope for the two correlations.

The somewhat poorer correlation for the line sampling data may be attributed
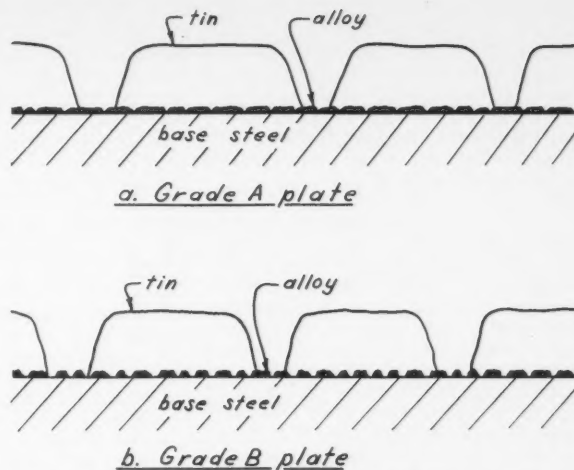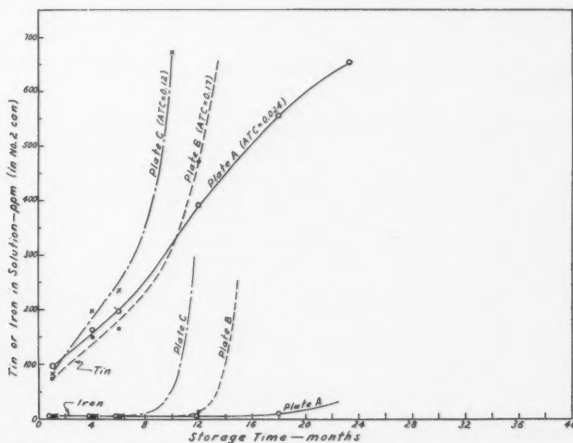
at least partly to the use of single ATC data and service life from individual cans, but it is believed that much of the difference in slope of the lines and degree of correlation may be attributed to variations in continuity of the tin coating, a factor not measured by ATC. The ATC measures galvanic corrosion caused by areas detinned to the alloy layer, but since much of the alloy is covered by tin during a large part of the container life, the degree of coverage afforded by the tin is also important. The relatively short service life for the higher ATC plates represented in Figure 3 could be due to generally poorer coverage of the high ATC alloy surface by the free tin coating than was the case with the line sampling plates. A suggestion of this is seen in the high ISV data observed in Figure 4 for the plates represented in the comparison of ATC with average performance, while most of the line sampling plates had ISV less than 20. Although ISV is dependent upon nature of the base steel, in many cases the amount of steel exposed is also a factor. Further evidence of the effect of tin coverage will
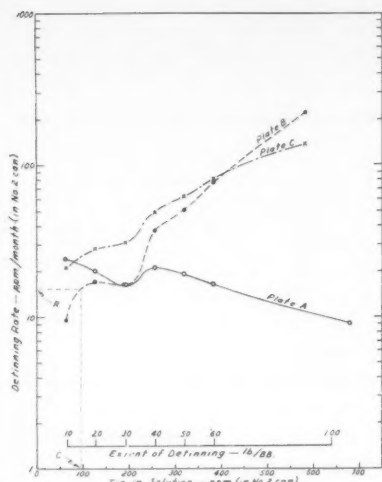
Figure 10—Rate of detinning in a No. 2 can at various stages of detinning, calculated from Progressive ATC test data and expressed as rate of tin pickup in the product.

Figure 11—Predicted corrosion of tin plate in pack tests, calculated from Progressive ATC data.

be presented in the discussion which follows.

A Theory of Tin Plate Corrosion

In the light of information from test pack analyses for tin and iron pickup in the product, and evidence obtained from work in connection with the ATC test, a theory of corrosion for tin plate by food products has been developed which fits accepted electrochemical theory. This theory provides an explanation for poor correlation between corrosion resistance and porosity measured at the tin surface reported in the past.

Corrosion in grapefruit juice and similar products is the result of galvanic couple action between the free tin coating and the steel or iron-tin alloy exposed at discontinuities in the tin layer. The rate at which tin is driven into solution is controlled by the size and electrochemical nature of the exposed cathodic areas. Until nearly all of the tin is consumed by the corrosion processes, both steel and alloy receive essentially complete cathodic protection.

Several methods have been described in the literature for measuring porosity of tin coatings,[5, 6, 7] but in view of the poor correlation observed between plate performance and porosity measurements, this factor has been considered of relatively minor importance to corrosion resistance.[3, 8] The discussion which follows provides a logical explanation for the poor correlation, and puts the importance of tin porosity in its proper perspective.

Theory of Relative Tin and Alloy Porosities

Using the ferricyanide test[7] as a rough measure of exposed steel, porosity tests were run at the tin and alloy surfaces of several No. 100 electrolytic plates. Although the results can be considered only roughly quantitative, it was apparent that more steel is exposed through the alloy layer than through the combined layers
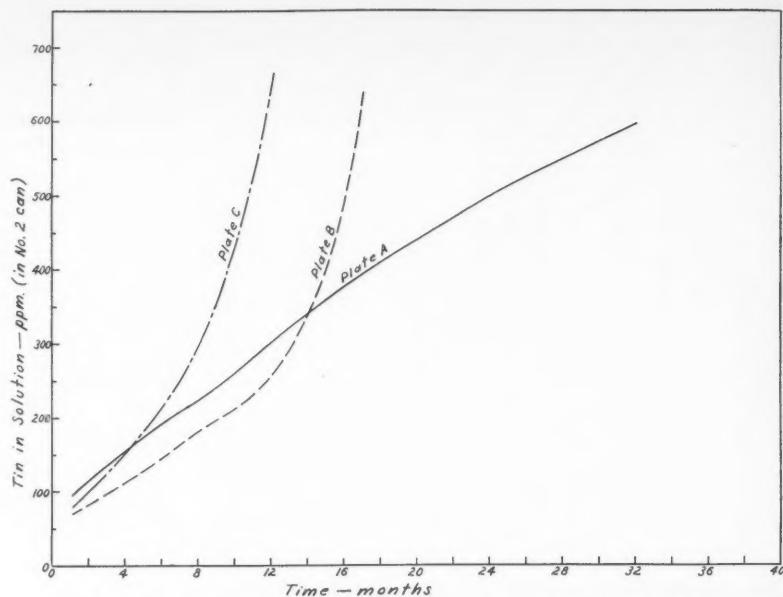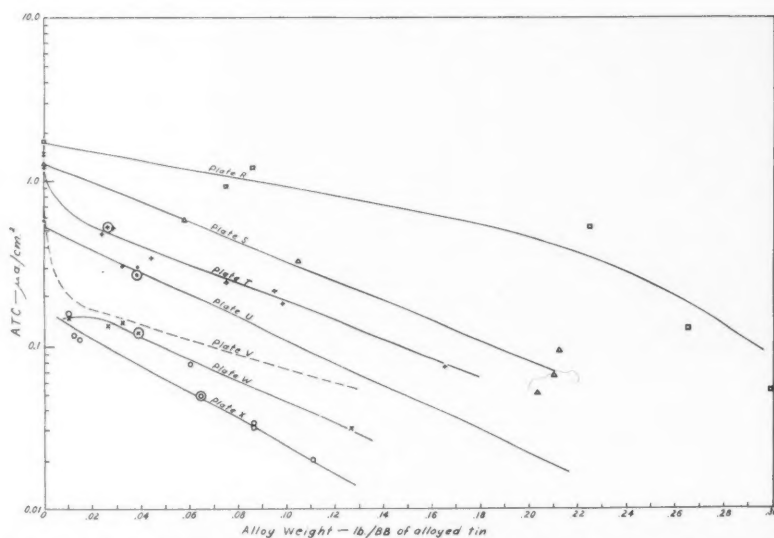
Figure 12—Effect of amount of iron-tin alloy on ATC, obtained from matte plates melted in the laboratory to various alloy weights, and from companion lots commercially melted (circled points).

of tin and alloy, especially so in the case of Grade B plates. This seems reasonable if the cross sections of tin plate surfaces are visualized as shown schematically in Figure 7. Pores in the tin layer do not always coincide with voids in the alloy, and tin actually contacts the steel surface where voids in the alloy are covered by tin. Either alloy or steel, or both, are exposed through the pores in the tin coating. The sketches are intended to indicate relative continuity of the alloys, and do not reflect their crystalline nature.

Typical differences in structure of the actual alloy layers of Grades A and B plates are illustrated by the electron photomicrographs in Figure 8. These were taken by a chromium shadowed carbon replica technique at the alloy surface exposed by detinning electrolytically in 5 percent NaOH. The Grade A plate shows finer alloy crystals and better coverage of the base steel than observed for the Grade B sample.

Covert and Uhlig[9] reported the corrosion potential for $FeSn_2$ in 0.1M citric acid as cathodic to both tin and steel, but because of its high hydrogen overvoltage they considered the alloy of minor importance in the galvanic couple reactions forcing tin into solution. Bright and Britton[10] have reported alloy potentials even more cathodic, but concluded that rapid cathodic polarization of the alloy results in very low currents upon coupling to tin.

Measurement of corrosion potentials of tin plate alloy surfaces in the ATC test indicate that the corrosion potential of the alloy surface, which is actually a mixed potential of the alloy and steel exposed through it, lies between those of tin and steel. The potential of the Grade A alloy surface approaches very closely the potential of tin. This discrepancy in alloy potentials reported by different investigators may be due either to differences in test media, or to the methods employed in sample preparation. More important, the high hydrogen overvoltage of the alloy was confirmed in grapefruit juice, indicating that exposed alloy contributes relatively little to galvanic corrosion of the tin.

It follows as a logical hypothesis that the rate of galvanic detinning in the products under consideration is determined mainly by the *amount and nature* of the steel exposed through the combined "screens" of tin and alloy. As detinning progresses and larger areas of alloy become exposed, the rate increases, the rate of acceleration being dependent upon the ATC at the alloy surface. The ATC measures the combined effect of alloy continuity and nature of the steel exposed through the alloy. The rate of detinning continues to increase as more and more of the alloy surface is exposed, the final rate being closely related to that calculated from ATC data and area of plate below the liquid level in the can, corrected for pack temperature and Sn^{++} concentration in the product. This line of reasoning leads to the following theory of corrosion for different grades of plate, which, as will be shown later in this paper, is supported by pack data and electrochemical test results.

In the case of Grade A plate (Figure 7a) the alloy is uniform and continuous, exposing very little base steel. The ATC in this case is low. Thus, regardless of tin porosity or amount of tin removed, the rate of detinning will be relatively low.

Grade B plates (Figure 7b) show relatively poor coverage by the alloy layer and higher ATC. A low porosity tin coating over such alloy would cover most of the exposed steel, resulting in a low initial rate of detinning. The factor which limits performance of such plate to the Grade B range is the increased rate of detinning which occurs when detinning progresses to the point where areas of the high ATC alloy surface become exposed. A plate having extremely good tin coverage could approach Grade A pack performance, even though the ATC at the alloy surface is not extremely low, because of the very low initial detinning rates.

Plates with corrosion resistance inferior to Grade B are those with high ATC and poor tin coverage. In this case the initial rate of detinning is higher than for Grade B plates, exposing the alloy earlier and at a faster rate. The result is early failure of cans made from such plate.

For both Grade A and B plates where very little steel is exposed initially through the combined tin and alloy layers the ISV would necessarily be low.

Also, plates with extremely high ISV would be expected to have relatively greater areas of steel exposed and would fall in the category of inferior plate having relatively high ATC and poor tin coverage which fails early in packs. This, in fact, is the case in commercial experience. However, since ISV is not determined solely by the amount of steel exposed, only large differences in ISV can be taken to indicate significant differences in coverage of the steel.

Supporting Pack Data

Tin and iron pickup data from actual pack tests support the theory of relative porosities described above. Figure 9 represents the amount of tin and iron in the product at various storage intervals for No. 2 cans[5] of grapefruit juice stored at 100 F. Each point represents the average of analyses from three cans. The rate of tin dissolution for Plate A (ATC = 0.024 μ amp/cm.²) was relatively constant; the inhibiting effect of increasing Sn^{++} concentration apparently compensated for increasing area of alloy exposed as detinning progressed. Plate B (ATC = 0.17 μ amp/cm.²) showed an initial rate comparable to that of plate A, with a marked increase in rate of tin pickup by the time 0.40 lb/BB of tin (260 ppm) had been dissolved from the plate surface. This corresponds to the amount of detinning required to expose visible areas of alloy on a No. 100 electrolytic tin plate surface. Plate C (ATC = 0.12 μ amp/cm.²) detinned faster from the very start, and showed a rate increase at 0.40 lb./BB of detinning similar to that for Plate B. Plate C is believed to be an example of a plate having poor tin coverage but relatively low ATC failing earlier than Plate B which has good tin coverage and higher ATC. Further evidence of this is presented in the section which follows.

The amount of iron in solution shows that the steel was protected from corrosion until nearly all of the tin had been removed from all plate surface in contact with the product.

Progressive ATC procedure

The same three plates discussed above were subjected to electrochemical tests designed to measure the galvanic detinning action at the plate surfaces with various amounts of tin removed. This was done to duplicate more closely the corrosion process in a tin plate can packed with grapefruit juice. The ATC procedure was modified slightly by using only 5ppm of added Sn^{++} to give higher corrosion currents on the tin plate surface and to provide conditions more favorable to anodic polarization of tin at the sample surface[4]. It is preferable to use a relatively large volume of juice to assure stable Sn^{++} concentration throughout the test. A tin to sample area ratio of 20:1 was employed to minimize anodic polarization of the tin electrode.

Samples were run with 0.10, 0.20, 0.30, 0.40, 0.50, and 0.60 lb/BB of the tin coat-

<hr>

[5] Cans were 3-7/16″ diam. x 4-9/16″. They contained 570 grams of grapefruit juice, with approximately 320 cm.² of plate surface below the liquid level.

ing removed electrolytically in 1N HCl, as well as with all free tin removed electrolytically in 5 percent NaOH. The initial determination was made with 0.10 lb/BB of tin removed since that amount of detinning occurs during packing of the can due to high temperatures and presence of a limited amount of oxygen. The partially detinned samples were coupled to the large tin electrode which then furnished most of the current required by exposed steel or alloy cathodic areas on the sample surface. Thus the couple current measured was approximately equal to the rate of galvanic detinning at the plate surface before coupling. Current densities obtained were corrected to 100 F (pack temperature) and to Sn^{++} concentrations equivalent to that in a No. 2 can detinned to the same degree. These corrections were made according to data for the effects of Sn^{++} concentration and temperature shown in Figures 13 and 14, respectively, which are discussed in Appendix B. Detinning rates, calculated on the basis of plate area below the liquid level and the amount of product in a No. 2 can, are plotted in Figure 10 against extent of detinning and the corresponding concentration of tin in solution in the can.

The rates with 0.10 lb/BB of tin removed fall in the order expected from the tin in solution after one month's storage in the test pack (Figure 9). Apparently the tin coverage of Plate A is such that much of the steel exposed through the alloy is also exposed through voids in the tin. As detinning progresses the increase in rate due to exposure of larger areas of the low ATC alloy is more than equaled by the inhibiting effect of increasing Sn^{++} concentration. The net result is a decrease in rate as detinning proceeds. Differences in initial rates for plates B and C are apparent. As in the pack test, the rate of detinning increases markedly for these plates at around 0.35 to 0.40 lb./BB of tin removed. A similar rate increase has been observed for other plates tested by the Progressive ATC procedure.

The curves in Figure 11, which predict relative pack performance, were calculated from the data in Figure 10. Taking C_1, the concentration of tin in the product at one month's storage in the actual pack test (Figure 9) as a starting point, the rate of detinning, R_1, corresponding to that concentration of tin in a can, is obtained from the appropriate curve as indicated in Figure 10. Assuming that the rate remains relatively constant for a period of one month, t, the concentration C_2 at the end of the second month is given by the equation:

$$C_2 = C_1 + tR_1 \qquad (3)$$

where C = concentration in ppm, and R = rate in ppm/month. It follows that at three months:

$$C_3 = C_2 + tR_2 = C_1 + t[R_1 + R_2]$$
$$\text{or} \quad C_n = C_1 + t$$
$$[R_1 + R_2 + R_3 \cdots + R_n - 1] \qquad (4)$$

where C_n is the concentration in ppm at any given month n, and R_n is the rate in ppm/month corresponding to the degree
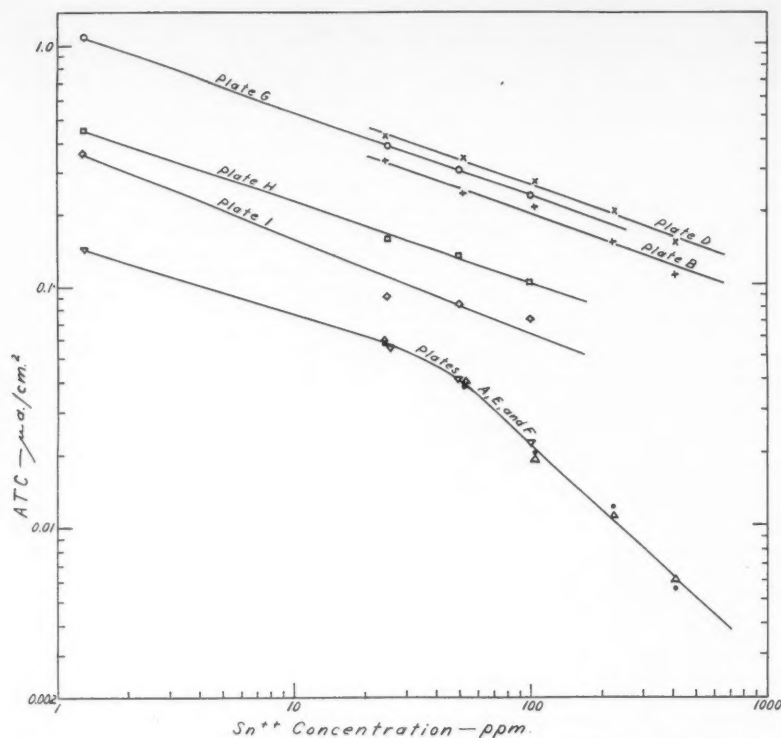
Figure 13—Effect of Sn++ concentration on ATC, determined at 79 F (26 C) from plates representing a range of ATC.

Figure 14—Effect of temperature on ATC, determined at 100 ppm Sn++ concentration from plates representing a range of ATC.

of detinning which gives that concentration of tin in the product. The curves in Figure 11 were obtained by computing C_n at one month intervals.

The similarity in shape of these curves to those shown in Figure 9 for an actual pack is quite striking even through the failure times do not coincide exactly. Two things could be responsible for these differences: (1) Damage to the tin and alloy layers at areas severely cold worked in forming the can (Table 1), or (2) the ring of alloy usually exposed at the liquid-headspace interface due to small amounts of headspace oxygen. Both of these factors would tend to increase the detinning rate slightly. Failure to measure 100 percent of the corosion current by the Progressive ATC method, or the use of constant rates for one month periods in calculating the curves may also be factors. However, it is apparent from both the shape of the curves and relative performance predicted that the currents measured by this modification of the ATC test are closely related to detinning rates in the pack test, and should be useful for predicting relative performance of various lots of plate. This test takes into account tin coverage, alloy coverage, and electrochemical behavior of the exposed steel in a typical food product, all of which affect the rate of galvanic corrosion. Further studies are in progress to establish a simplified procedure for this type of test.

Porosity Measurements

The usual tin plate porosity tests are not suitable for measuring porosity as it affects galvanic detinning by food prod-

ucts. Attempts to evaluate initial porosity of tin plate by means of the thiocyanate[6] and ferricyanide[7] tests have produced inconclusive results, with indications that both the alloy and base steel are attacked when testing at the tin surface. Some work has been done to select a test medium in which the tin-alloy-steel potential relationships are such that only exposed steel is measured. However, caution must be exercised in interpreting the results of such tests since neither the continuity of the alloy covered by the tin nor the cathodic behavior of exposed steel in a typical product is measured. Only in a test such as the Progressive ATC are all factors considered, including the effect of partial detinning.

Application of the ATC to Tin Plate Research

The ATC has been shown to measure properties at the alloy surface important to Grade A corrosion resistance. It would appear, therefore, that the test could be used for evaluating research efforts in tin plate manufacture intended to improve corrosion resistance. There are, however, certain factors which must be considered in interpreting the data.

Effect of Alloy Weight on ATC

The correlation of ATC with pack performance was established without regard for amount of iron-tin alloy. Although limited laboratory work with heavier alloys had indicated an effect on ATC, the extent of this effect was first observed by Carter and Butler[11] in work which indicated a marked decrease in ATC with increasing alloy weights.
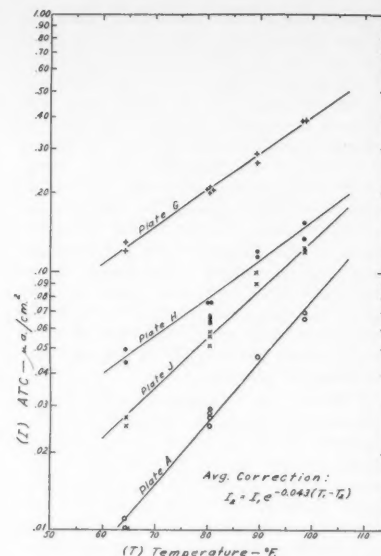
Additional studies were conducted to establish the effect for a number of plates of varying quality.

The data obtained are shown in Figure 12. Included are data from six commercial matte (unmelted) plates (0 to 0.010 lb/BB of alloyed tin) as well as for adjacent samples of the same plates resistance melted in the laboratory to various alloy weights. Also shown for plates, T, U, W, and X are the values (circled points) from commercially melted plate from the same coil from which the matte samples were taken; these points fall on the line obtained from the samples resistance melted in the laboratory. The line for Plate V was established from a large number of points which are not shown. All alloy weights, determined by the method of Kunze and Willey,[12] are expressed as lb/BB of tin in the alloy. Data from a larger number of samples for a given plate, which would of necessity represent a larger area of plate, would fall along the lines shown but with more scatter than is apparent from the data plotted.

Interpretation of Data

It appears that each plate tested exhibits its own ATC-alloy weight line, with most of them showing similar slopes, and the position of the line indicating plate quality. Plate R which had extremely high ATC is a plate which is failing early in test packs; plate X is of commercial Grade A quality.

Pack data are not yet available to demonstrate whether the lower ATC at high alloy weights is a true indication of improved corrosion resistance. It is apparent, however, from the data in Figure 12 that only by increasing alloy thickness well beyond commercially acceptable limits[6] is the ATC of Grade

(6) Sufficient free tin is required on the No. 25 side of No. 100-25 differential plate to avoid difficulties in soldering and other fabricating operations. The amount of alloy on commercial electrolytic plate is normally held within the range of 0.04-0.08 lb./BB to meet this requirement.

B plate reduced to values equivalent to those observed for Grade A plate bearing normal alloys. Poor correlation has been obtained between ATC and service life for hot dipped and mender[7] plates, which bear relatively heavy alloys; this suggests that increasing alloy weights beyond present commercial limits would not give as great an improvement in performance as is indicated by ATC. Damage to the heavy alloys in can fabrication is believed to be responsible for the poor correlation.

Values obtained by detinning the matte plates, sometimes referred to as STC (Steel-Tin Current), in many cases fall on or near the end of the ATC-alloy weight line, although exceptions are noted. Response similar to that of plate V (Figure 12) has been observed in several instances. STC determinations may be used to give a rough measure of the effect of steel preparation and plating. However, for reliable information the steel should be plated, melted, and evaluated in terms of ATC and alloy weight, aiming for alloys in the commercial range. If the ATC-alloy weight relationship has been established for the plate in question, it may be used to correct ATC data to the alloy weight which would be aimed for in commercial production.

The ATC test can be valuable in establishing tin plate manufacturing practices which produce conditions at the alloy surface favorable to Grade A corrosion resistance. Such factors were evaluated formerly only through pack tests. Development of a standard procedure for the Progressive ATC modification will permit evaluation of factors affecting coverage by the tin coating.

Summary

A new test has been described which evaluates the corrosion resistance of electrolytic tin plate for a class of food products. It consists of the measurement of the current flowing between tin plate, detinned to the alloy, and pure tin coupled in deaerated grapefruit juice.

Alloy-Tin Couple test data have been shown to correlate well with pack performance, with indications that low ATC assures good corrosion resistance. The ATC provides in one day a measure of certain factors in plate quality which formerly required as long as two years in accelerated pack tests. This electrochemical test is believed to be a measure of the effect of alloy discontinuities and nature of the base steel exposed through the alloy, as related to galvanic detinning in grapefruit juice and similar products. Variations in continuity of the iron-tin alloy layer have been demonstrated by electron photomicrographs.

A theory of tin plate corrosion, based on the relative importance of tin and alloy porosities, has been described which explains the lack of correlation between tin porosity and pack performance observed in the past, and demonstrates that ATC alone cannot be considered an over-all corrosion test.

Pack data support the theory that initial detinning is determined by the amount and nature of exposed steel as seen through the combined tin and alloy layers, and as detinning progresses the ATC at the alloy surface becomes increasingly important. A modification of the ATC test, which takes into account continuity of both the tin and alloy layers, and nature of the base steel, produced detinning curves closely resembling those observed for the test pack. The usual methods for measuring porosity have been found unsuitable for determining steel exposed through the combined tin and alloy layers.

The ATC is shown to be affected by the amount of iron-tin alloy, a factor which must be considered in interpretation of data from tin plate research. Used as a research tool for rapidly evaluating the corrosion resistance of experimental plates, the ATC test can speed progress toward production of Grade A plate.

APPENDIX A—DETAILED ATC PROCEDURE

Test Cell

A borosilicate test cell (Figure 1) of one liter capacity is fitted with a plastic top containing a series of $5/8$-inch diameter holes through which samples, a tin electrode, a reference electrode, and a thermometer are inserted. Stoppers or grommets cut from $1/4$-inch silicone rubber sheet (Sirvene Division of Chicago Rawhide Manufacturing Co.) are used to effect a seal around these items. The seal between the top and the cell is made by means of a polychloroprene "O" ring gasket. All rubber parts used in the cell are treated in boiling 10 percent NaOH for five minutes and rinsed thoroughly prior to use in the test. Provision is made in the top of the test cell for a slow but continuous flow of nitrogen gas through the headspace. The gas is bubbled through deionized water before passing through the cell to minimize evaporation of the test solution; a slight positive pressure is maintained by bubbling the effluent gas through $1/2$-inch of dibutyl phthalate. High purity tank nitrogen (Linde high purity dry, or equivalent) is used without further purification. The cell is designed with relatively small openings so that the samples can be changed without danger of air contamination by merely increasing the flow of nitrogen through the headspace. A simple coil of glass tubing is provided for rapid cooling, and a polytetraefluoroethylene covered magnet permits stirring.

Care must be exercised to prevent mold growth or fermentation of the juice. Fermentation causes high couple currents. Thorough cleaning of all cell parts and sterilization with 70 vol. percent ethanol (including samples) has given satisfactory results. An alternate method consists of adding 0.5 gm/liter of potassium sorbate to the test medium. This has been effective in preventing spoilage for periods of 4 weeks or longer and has no effect on ATC. A single batch of juice should be used no longer

than 3 to 4 weeks to avoid excessive build-up of Sn^{++} which would give low ATC. The rate of increase in Sn^{++} concentration is dependent upon the average total couple current and the volume of solution used.

Test Medium and Tin Electrode

The test medium consists of commercial frozen concentrated grapefruit juice (sweetened) diluted 3:1 with deionized water. The resulting solution is deaerated by heating to boiling, after which the cell is filled and closed, and nitrogen is flushed through the headspace (900 ml of solution is used leaving $1/4$-inch headspace). After 5 minutes, cold water is run through the glass coil and the juice is stirred to effect rapid cooling. This tends to minimize settling out of the pulp.

A coil of pure tin wire of approximately 100 cm.^{2} area is inserted in the cell after the juice has cooled. This is considered desirable to eliminate the possibility of dissolving some tin in the hot juice. The tin electrode is cleaned cathodically in 0.5 percent Na_2CO_3 solution, rinsed with deionized water, and dried with acetone before being placed in the cell. The potential of the tin electrode in the grapefruit juice of pH 3.25 is approximately —755 mv. Upon adding 0.190 gm/liter of $SnCl_2 \cdot 2H_2O$ to the grapefruit juice to give 100 ppm of Sn^{++} in solution, the tin electrode potential shifts to approximately —705 mv thus serving as a rough check for Sn^{++} concentration. Although the potentials in some batches of juice are slightly lower (more cathodic), the shift upon adding Sn^{++} is the same. No difference in ATC has been observed with such juices. All potential measurements are made with a Beckman Model G pH meter using a 0.1N calomel reference electrode.

Sample Preparation

The tin plate samples, cut to 7/16-inch x $4\frac{1}{2}$-inch strips, are degreased in acetone, then cleaned electrolytically in 0.5 percent Na_2CO_3 solution (carbon anode). Using 10 v DC, a treatment of 0.1 sec. anodic, 2 sec. cathodic, 0.1 sec. anodic, and 2 sec. cathodic is quite effective in removing all traces of impurity as indicated by no water break. The anodic flash in this treatment greatly facilitates the cathodic removal of any oxide on the surface. After rinsing in deionized water the sample is ready to be detinned.

A constant voltage method for detinning has been devised which is an adaptation of a method described by Hothersall and Bradshaw.[13] In this method a low resistance shunt (0.1 ohm) is placed in parallel with the detinning circuit to assure constant voltage. The cathodically cleaned tin plate sample is detinned electrolytically in 5 percent NaOH at a constant 0.40 v, using a stainless steel cathode. The area of the stainless steel cathode is kept large compared to the area being detinned (5 to 10:1) to give a high anode current density and rapid detinning rate. As detinning nears completion it is likely that a small area or a few isolated spots will be slow to detin. Reducing the voltage to 0.20 v

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(7) A "Mender" is electrolytic tin plate retinned by the hot dip process to reclaim material which has been rejected because of superficial coating defects.

at this point speeds up markedly the detinning of these last few spots. It has been found convenient to detin several samples simultaneously, all connected in parallel to the power source. When this is done it is necessary to reduce the voltage only for the last sample remaining in the bath. Samples should be removed from the bath with power on to prevent reversal of the current and replating of tin as a result of the primary cell effect. It is recommended that samples be left in the detinning bath no longer than 5 minutes.

The detinned samples are masked with microcrystalline wax (140-145 F) to expose a given test area. This may be done by hand brushing or by mechanical methods, provided the test surface is not damaged or contaminated in the process. A die for applying an outline of wax exposing a 2.33 cm.² test area was used for much of the work reported in this paper. After the test area has been outlined the sample is manually waxed to a thin plastic backing (1/16-inch x 9/16-inch x 3¼-inch) to complete the masking. This procedure assures complete coverage of the steel edges.

Current Measurements

The test sample is coupled to the tin electrode before inserting it into the cell to assure protection of the alloy surface from corrosion. All samples are coupled to the single tin electrode. The test cell should be insulated from vibration which would give high ATC due to the stirring effect. After twenty hours the current flowing to each sample is measured by inserting a low resistance galvanometer into the circuit as shown in Figure 2. All current measurements were made with a Model 2430-C Leeds and Northrop galvanometer. ATC values are calculated by dividing couple current by sample area. A test temperature of 79 F (26 C) is used as standard.

APPENDIX B—FACTORS IMPORTANT TO THE TEST

Test Medium

The use of a typical food product as test medium, or a synthetic medium closely resembling the product, is essential. Differences between good and poor plates were observed in 1N HCl and 0.1M citrate buffer, pH 3.2, but correlation with pack results was not good. Attempts to formulate a synthetic medium simulating grapefruit juice have been only partially successful, with indications that the juice is composed of many substances which can affect corrosion, some of which act synergistically.

Oxygen-free System

The nitrogen atmosphere, which simulates oxygen-free container conditions, is required for meaningful results. Admitting air to the cell increases the couple currents markedly, giving no separation between good and poor plates.

Sn++ Concentration

Sn^{++} is added to the test medium because of its known effect on corrosion and couple currents, 100 ppm being chosen to provide stable conditions which would not be affected appreciably by small increases in Sn^{++}. This allows use of the same solution for a large number of samples.

The actual effect of Sn^{++} concentration on ATC is shown in Figure 13. Eight plates were tested at various Sn^{++} concentrations ranging from 1.3 to 410 ppm; each point represents the average of two ATC values from a single plate. For Sn^{++} concentrations above 50 ppm the effect on ATC is greater for the three Grade A plates (A, E, and F) than for the higher ATC plates. This exceptional response to Sn^{++} may be partially responsible for the good performance of Grade A plates tested. This effect would not be detected if 50 ppm Sn^{++} or less were used in the test.

Sample Preparation

Detinning electrolytically in 5 percent NaOH exposes the alloy surface without attacking it, providing a surface similar to that exposed in a can where the alloy has been protected cathodically by coupling with tin. The back and edges of the sample must be masked to expose only the test area. Since ATC is measured as current density, the actual area is not critical, provided the resulting currents are not high enough to change the Sn^{++} concentration of the cell or to be affected by the IR drop in the current measuring system. Sample areas ranging from 0.50 to 4.0 cm.² have shown no effect on ATC.

Protection of the Sample

Coupling to tin *before* immersion of the sample in the test cell simulates container conditions where the alloy and steel are always protected. Short exposure of the alloy uncoupled allows corrosion to occur which changes its nature appreciably, resulting in high ATC values.

Size of Tin Electrode

A large tin electrode is employed to approximate the large tin to steel area ratio existing in a tin plate can. Although

the tin anode does not polarize easily in the presence of 100 ppm Sn^{++}, a large electrode is considered desirable to prevent polarization of the tin in the early stages of the test when currents are relatively high. Tin to sample area ratios as low as 3:1 have been used successfully. No effort has been made to determine the minimum ratio acceptable. The large tin to sample area ratio becomes more important at lower Sn^{++} concentrations.

Effect of Test Temperature

The dependence of ATC on test temperature is illustrated in Figure 14. Four plates, representing four levels of corrosion resistance, were run at several temperatures between 64 and 100 F. The results indicate a straight line relationship between log ATC and temperature, with a steeper slope apparent for the better plates. The average temperature effect can be described by the equation:

$$I_2 = I_1 e^{-0.043(T_1 - T_2)}$$

where I = ATC (μ amp/cm.²), and T = temperature (degrees F). Experience with a large number of plates has shown that this average correction may be used over a 10 F range without introducing serious error.

The 2½ to 5 fold difference in ATC at 70 and 100 F corresponds very closely to the differences in performance observed in test packs stored at those temperatures.

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Any discussion of this article not published above will appear in June, 1961 issue.

Coupling Shift and Hydrogen Overvoltage
In the Protection of Steel by Tin*

By E. L. KOEHLER

About the Author

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Introduction

ON THE interior surface of the tin plate can, tin is known to afford sacrificial protection to areas of exposed steel. This prevents perforations. Sacrificial protection in itself, however, is of no help in retarding the occurence of "hydrogen swells" or "springers" resulting from the evolution of hydrogen inside the can. On the contrary, the simple concept of sacrificial protection would require an increase in the rate of hydrogen evolution concurrent with the protection of the steel.[1]

A large part of the success of the tin can may be ascribed to the fact that more than simple sacrificial protection is involved; protection of steel through "coupling" with metallic tin produces a marked decrease in rate of hydrogen evolution from the steel exposed. The decrease in hydrogen evolution from steel by coupling to tin has been shown to be too great to be attributable to simple inhibition by dissolved tin.[2] Furthermore, the effect has been observed in at least one case in which dissolved tin is not effective as an inhibitor.[3]

It was also demonstrated that coupling to tin causes a slow shift of the steel potential in the positive (noble) direction. Further, on "decoupling"[1], the steel potential slowly shifts back in the negative (active) direction. The slow shift in potential on coupling tin to steel has been called "coupling shift." It has been found difficult, if not impossible, to reconcile the existence of coupling shift with accepted theory for the corrosion of iron in weak acid media. This investigation was undertaken therefore, to confirm the existence of the effect and to investigate the mechanisms involved.

Experimental

All experiments were conducted with "T" cells, illustrated in Figure 1. The ground ends of the 2-inch horizontal length of 30 mm glass tubing were dipped in microcrystalline wax and a specimen of steel and a specimen of chemically-pure, rolled tin were sealed to opposite ends. The assembly was held together with a "C" clamp. Specimens were backed up with pieces of stiff nickel sheet faced with $\frac{3}{32}$-inch insulating rubber. The area of specimen exposed was measured to average 5.31 sq cm. Hydrogen evolved inside the cell collected in the domed top, forcing liquid up the graduated pipette where it could be measured. Cell tops with three sizes of pipettes were used, 1 ml, 2 ml, and 5 ml depending on the requirements for the individual test.

A saturated calomel reference electrode was used for each cell. The enclosing bridge of this electrode was made of 8 mm tubing with a fine crack in the sealed bottom. The electrode was connected to the vertical arm of the three-way stopcock by modified polyvinyl chloride tubing. Even though the diffusion of chloride out of these electrodes occurs at only a very slow rate, the stopcock was kept closed except when making measurements. The stopcock was used also in filling and in adjusting the volume level of the test cell. The rubber expansion bulb at the top prevented air from diffusing in. In a cell with this simple geometric design, it was considered easier to correct for IR drop in the electrolyte than to use a Luggin capillary.

Steel specimens were all cut from one randomly-selected 8-inch wide strip of type MR steel.[2] Steel specimens were electrocleaned in hot sodium orthosilicate solution. Tin specimens were treated in cold, concentrated hydrochloric acid prior to use.

The corrosive medium used was pH 3.5 citrate buffer (made 0.05M in sum of citric acid and sodium citrate). An addition of 50 ppm Sn^{++} was made either as the sulfate or chloride. It was found that at this concentration, the anion made little difference. Results reported here are for the stannous sulfate addition. The solution was flushed with hydrogen for two hours prior to filling the cells. Cells were flushed with air-free nitrogen and filled in such a manner as to keep out all air.

After filling, cells were placed on shelves in a constant-temperature room maintained at 37.8 C (100 F). Cell volume readings were adjusted to zero after two hours at this temperature. The constant temperature room was especially wired so that all desired electrical readings could be made off panel boards on the outside of the room.

All tests were run at least in triplicate and were repeated at least once. Where weight loss data were required, a series of eight cells was set up; these were discontinued at varying time intervals to determine the rate of weight loss.

Abstract

Evidence is presented to further substantiate the existence of a "coupling shift" for the tin-steel couple in weak acid media. By virtue of the shift, tin is able to sacrificially protect steel concurrent with a greatly diminished rate of hydrogen evolution. Since an explanation of the phenomenon does not seem possible on the basis of existing corrosion theory, additional experimental evidence was sought to elucidate the mechanism. Polarization curves were determined with automatic equipment, enabling this to be done more rapidly and reproducibly than is usually possible. Results indicate a mechanism in which corrosion rate and corrosion potential are determined entirely on the basis of hydrogen reactions occurring on the metal surface. Coupling shift is associated with an increased hydrogen overvoltage.   5.2.1, 3.6.8

All potentials were measured with the potentiostat used in polarization studies. This special instrument, built by Leeds and Northrup, consists primarily of an adjustable-zero, adjustable-range, high-impedance, recording potentiometer. A front-set control point operates a polarizing unit through a position-type electronic control so as to provide such a potential across the test electrode (steel) and the auxiliary electrode (tin) as to polarize the steel to the set potential with respect to the saturated calomel reference elecrode. The potential control point was equipped with a variable drive to enable the potential to be changed at a selected linear rate with respect to time.

In the polarization studies, current from the potentiostat was passed through the cell with the steel specimen as test electrode and the tin specimen at the other end of the cell as auxiliary electrode. In polarization studies involving cells in which the tin and steel coupled, the specimens were first "decoupled" until a steady potential for the steel was attained (generally five minutes); then polarization curves for the steel were determined as above. Currents passing through the cell in the polarization studies were measured with a recording instrument, an L & N Electro-

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* Submitted for publication May 3, 1960.

[1] In this paper "decoupling" refers to breaking electrical contact in a tin-steel couple. "Uncoupled" steel means simply steel which is not coupled to tin.
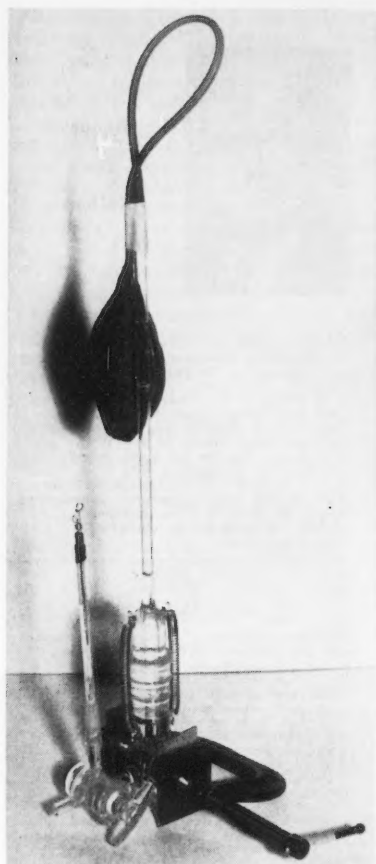
[2] Type MR steel has the following chemical specifications: C, 0.12 percent max; Mn, 0.20-0.60 percent; Si, 0.01 percent max; S, 0.05 percent max; P, 0.02 percent max; Cu, 0.20 percent max.

Figure 1—"T" Cell assembled as in test.

Figure 2—Instruments for automatically plotting polarization curves.

chemograph equipped with special current ranges and a switch to cut out the self-contained polarizer. This is a zero-resistance current measuring device. Since the potentiostat provided a linear rate of change of potential with respect to time, selection of a suitable chart speed on the current recorder enabled polarization curves to be directly plotted on the curent recorder chart.

Rate of polarization in the data reported here was 25 mv per minute. Data obtained were highly reproducible. In a few cases where a direct comparison was made, it was found that a polarization rate of 10 mv per minute gave the identical results. Polarization curves reported here do not show experimental points because the data were secured in the form of a continuous curve. Instruments used, together with a panel board on the exterior of the constant temperature room are shown in Figure 2.

Galvanic currents between tin and steel in coupled tests were measured with a multiple-range, multi-point, zero-resistance recorder, capable of taking sets of readings automatically at any pre-selected time interval.

Results and Discussion

After an induction period, hydrogen evolves from a specimen of steel totally immersed in citric acid solution at a rate equivalent to the rate of solution of the steel[2]. In the tests conducted here, the specimens were not fully immersed; an area on one side of the specimen only was in contact with the corrosive medium. This is more closely representative of the steel which may be exposed to the corrosive medium on the interior of a can. It has long been appreciated that part of the hydrogen produced as the result of corrosion on one side of a steel sheet diffuses out of the other side[4]. Under such conditions, the rate of solution of the steel is greater than the measured rate of hydrogen evolution from the corroding surface by an amount equal to the rate of hydrogen diffusion away from the corroding surface through the steel.

Figure 3 indicates the measured evolved hydrogen and the hydrogen equivalent to the weight loss for an uncoupled steel specimen on a "T" cell filled with pH 3.5 citrate buffer with 50 ppm Sn++ as stannous sulfate. It is seen that under conditions of the test the equivalent of the rate of weight loss was only slightly, if at all, greater than the measured evolved hydrogen, indicating a low rate of hydrogen diffusion through the steel. The amount of hydrogen evolved from the tin in these tests was found to be negligible.

In a parallel test to that illustrated in Figure 3, the tin and steel specimens on opposite sides of the "T" cells were electrically coupled and the resulting hydrogen volume and weight loss results
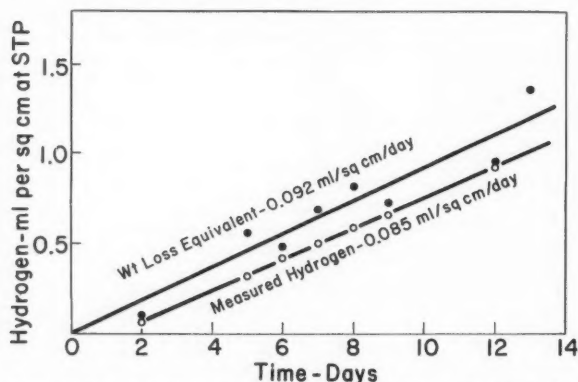
Figure 3—Rate of hydrogen evolution from steel corroded on one side at 37.8 C (100F) by pH 3.5 citrate buffer with 50 ppm Sn++, together with hydrogen equivalent of the steel weight loss.
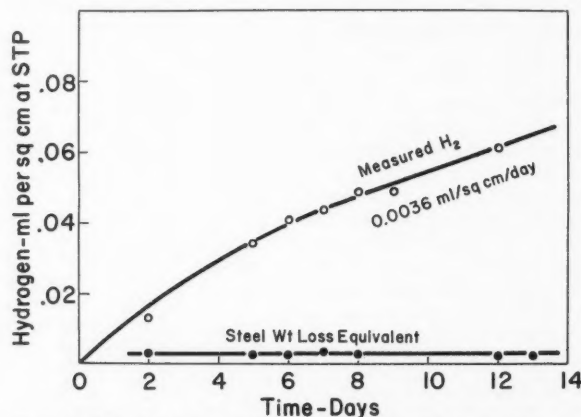
Figure 4—Rate of hydrogen evolution from steel coupled to an equal area of tin, corroded on one side at 37.8C (100F) by pH 3.5 citrate buffer with 50 ppm Sn++, together with hydrogen equivalent of the steel weight loss.
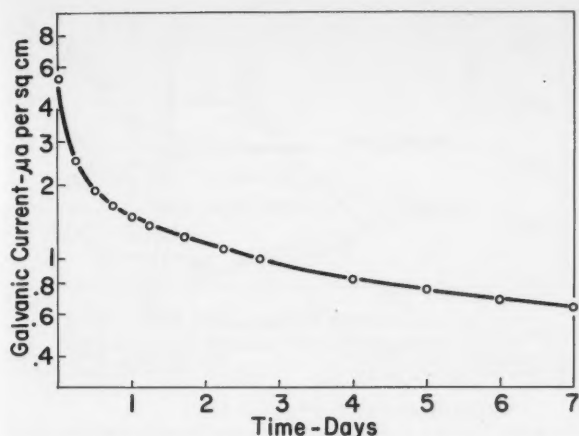
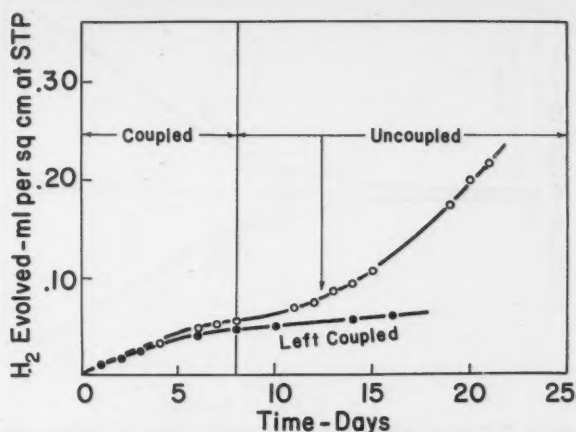Figure 5—Average galvanic current between tin and steel under conditions of test in Figure 4.

Figure 6—Effect of uncoupling after eight days on rate of hydrogen evolution. Corroded on one side by pH 3.5 citrate buffer solution with 50 ppm Sn⁺⁺. All specimens coupled for eight days to equal area of tin after which one group was uncoupled; the other group was left coupled.

are indicated in Figure 4. After seven days, hydrogen evolution occurred at a steady rate of 0.0036 ml per sq cm per day—less than five percent of the rate from uncoupled steel. Weight loss results indicate that beyond a small initial loss, the steel was fully protected and that any corrosion for the tin-steel couple here involved only galvanic action between the tin as anode and the steel as cathode.

Average galvanic current measurements as a function of time are indicated in Figure 5. By seven days, the curve has practically levelled out, approaching a level of approximately 0.56 μ amp per sq cm. This can readily be converted to ml H_2 at STP per sq cm per day by multiplying by 0.0100. The rate of galvanic tin solution therefore approaches 0.0056 ml H_2 per sq cm per day equivalent as compared to 0.0036 measured evolved hydrogen in the cells.

The decrease in the rate of hydrogen evolution on coupling to tin has been explained in terms of "coupling shift." Evidence of the existence of such an effect as distinct from inhibition by dissolved tin has been cited before. However, the data presented in Figure 6 are perhaps more directly illustrative. They show that if the steel is decoupled from the tin, the rate of hydrogen evolution slowly reverts to that characteristic of the uncoupled state. As indicated earlier[2] the potential also approaches that characteristic of the uncoupled state. This is, therefore, not simple inhibition by dissolved tin, although dissolved tin may be involved.

Current concepts of mixed potential theory envision the corrosion potential and the corrosion rate as determined by the point of intersection of independent polarization curves for the oxidation and reduction partial reactions. For steel corroding by hydrogen evolution in acid media, the polarization curves are considered to represent the oxidation of iron and the reduction of hydrogen on the metal specimen, reverse reactions being

considered negligible. These independent Tafel-type curves are of the form:

$$\eta = \pm \beta \log \frac{i}{i_o}$$

where

    $\eta =$ the overvoltage
    $\beta =$ a constant, the slope
    $i =$ current density
    $i_o =$ a constant, exchange current density at the reversible potential

Typical schematic polarization curves are illustrated in Figure 7. Curve ABC is the cathodic polarization curve for the reduction of hydrogen on the specimen. In segment BC the applied current is so great that the effect of local action currents is negligible. Extrapolating this curve back to the corrosion potential gives i_{corr}, the current equivalent to the rate of corrosion of the specimen. Theoretically the anodic polarization curve should be subject to the same analysis. Actually it has been found experimentally possible to determine accurately the polarization curve ABC and to determine accurately the corrosion rate by extrapolating to the corrosion potential. Previously, it has not been possible to do this with the anodic polarization curve as this curve has been found difficult to determine.[5, 6]

Figure 8 shows typical instrumentally-plotted polarization curves for uncoupled steel and for the steel of a tin-steel couple after decoupling. The cathodic polarization curve for uncoupled steel, 1C, has the expected slope. In individual tests, some variation was found in this slope with some values as low as 0.092 and some as high as 0.112 being obtained. The intercept with the corrosion potential is indicated to occur at 8.4 μ amp per sq cm. From Figure 3 it can be determined that the current equivalent to the rate of measured hydrogen evolution under these conditions is 8.5 μ amp per sq cm; the current equivalent to the rate of dissolution of the steel is indicated to be 9.2 μ amp per sq cm.

The potential of "decoupled" steel in Figure 8 for the test shown is —0.562 v.

The difference between this and the value for uncoupled steel, —0.614 v, represents the extent of coupling shift.

The slope of cathodic curve 2C is the same as 1C, within experimental variations. The value of i_o for 2C is however lower, indicating that the activation energy for the rate-determining step in the hydrogen overvoltage curve is higher for steel in the decoupled state than in the uncoupled state. The indicated shift in cathodic polarization curve for the decoupled state parallels the decreasing galvanic currents between tin and steel in the time it takes to develop a coupling shift as has been indicated in Figures 4 and 5. The shift of cathodic polarization curve in coupling shift is contrasted with the inhibiting effect of dissolved tin. Dissolved tin is known to be an anodic inhibitor[7] and it can be shown to have little effect on the position of the cathodic polarization curve below the point at which tin starts to plate out.

It is noted that in cathodic polarization curve 2C, the current suddenly increases, indicating a sudden increase in the rate of cathodic reduction. Interesting decay curves are obtained if polarization is carried beyond this point. These are illustrated in Figure 9. If the specimen is polarized just beyond —0.650 volt, curve A, there is a slight break in the curve at about —0.625 volt. If polarized to —0.710 volt, curve B, the decay curve levels out for a fairly long time before returning to the potential of the decoupled specimen. If polarized to a somewhat lower potential but held there for three minutes, curve C, the specimen remains at —0.625 volt even longer. Evidence appears quite strong that this effect is produced by the plating-out of tin on the steel.

No difficulty at all was found in obtaining instrumentally-plotted anodic polarization curves. These met all the criteria commonly ascribed to valid polarization curves: they were highly reproducible, they were of the expected form (Tafel-type), and they produced very little hysteresis—in fact, the speci-
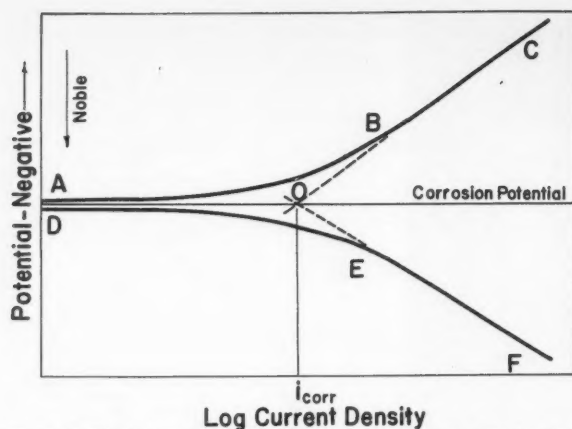
Figure 7—Classical representation of relationship between activation type polarization curves, corrosion current and corrosion potential.

Figure 8—Polarization curves for uncoupled and decoupled steel
1C - Uncoupled Steel, Cathodic   1A - Uncoupled Steel, Anodic
2C - Decoupled Steel, Cathodic   2A - Decoupled Steel, Anodic

men returned to the corrosion potential faster than after a cathodic polarization curve.

Curve 1A is typical of the anodic polarization curves obtained on uncoupled steel although the value of 0.022 v for β_a represents the highest rather than the average. In most curves the slope was found to be 0.020 v. The most noteworthy feature of the anodic polarization curves was found to be that the extrapolated Tafel curve always intersects the corrosion potential at a current density much lower than that equivalent to the corrosion rate. This intersection for curve 1A (Figure 8) occurs at 3.9 μ amp. If this is to be considered as an iron curve, intersection should occur no lower than and possibly above 8.4 μ amp. In addition, the slope is less than would be expected, as by calculation from the cathodic polarization data. In view of the high degree of reproducibility and the true Tafel form obtainable one might wonder whether this is truly a curve representative of the anodic oxidation of iron. The only alternative reaction would seem to be the re-oxidation of hydrogen from the steel.

It appears rather hopeless to explain either by simple mixed potential theory or local cell theory just how the coupling shift can be possible. This plus the nature of the anodic polarization curves obtained would lead one to wonder about the applicability of conventional mixed potential theory in this case. It would appear more reasonable to attempt some type of explanation by abandonment of the classical mixed potential concept that the anodic and cathodic processes are mutually independent and to admit the possibility of interaction between these processes.

There would seem to be some grounds for doubting the mixed potential principle of mutual independence of the anodic and cathodic partial reactions on the basis of logic alone. Consider, for example, iron corroding in acid solution where the whole surface of the corroding specimen seems available for the cathodic reaction. The anodic process does not seem to have any effect. Consider next a specimen of unit area

and visualize this as associated with a certain Tafel-type anodic polarization curve. This curve must certainly be area sensitive; with a specimen only half as big, only half as much current would be required to produce the same polarization. Starting again with the full unit area and evolving hydrogen on the specimen at such a rate as to give a coverage of one-half, it again should only take half the current to provide equal anodic polarization. This logic would infer that the cathodic process should produce the equivalent of anodic polarization.

It would be easy to make a mistake in logic. It is not difficult, however, to obtain substantiating experimental evidence. In fact it is difficult for an experimenter in hydrogen evolution corrosion to avoid obtaining some such evidence. Because of the great utility of the mixed potential concept, there has been little incentive to introduce complications. The mixed potential concept works in many cases because it is made to work by shifting the anodic polarization curve to any position needed to fit the picture. For many purposes no objection can be taken to this practice; occasionally, however, situations are encountered which are difficult to explain.

For example, many years ago the author found that different samples of steel, such as used in the production of tin plate, are dissolved in 6N hydrochloric acid at 90 C at varying rates, but that they all have the same corrosion potential. Since it was easily demonstrated that the variations in corrosion rate corresponded to variations in cathodic polarization curve, this would infer that either (1) the corrosion potential was an accident, (2) the anodic polarization curves were roughly parallel to the current density axis, or (3) there was a relationship between the anodic polarization curve and the cathodic polarization curve. It scarcely seemed possible that the same corrosion potential for so many different samples could be an accident. At the same time in a series of tests in which the specimens were allowed to corrode at varying applied currents it was found that small applied current produced no de-
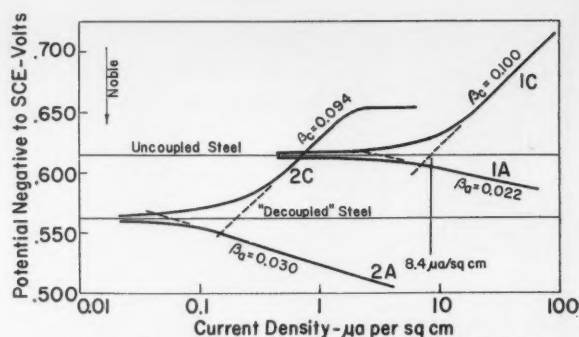
tectable effect on the corrosion rate. This would infer that the anodic polarization curve was almost parallel to the potential axis. Since this was impossible to reconcile with the previous observation, it seemed to follow that the cathodic processes were responsible for both cathodic and anodic polarization. The major point remaining seemed to be just what factors determined the corrosion potential.

Stern and Ross encountered a similar situation in accounting for the corrosion behavior of iron in acid NaCl solution at pH 1 to 4.8 [8] Their analysis showed that anodic polarization must exhibit an $\frac{RT}{F}$ dependence on pH. They suggested that the pH dependence of the corrosion rate and corrosion potential of iron may be explained as a decrease in anodic area with an increase in hydrogen activity on the surface. While they did not pursue this explanation further, this again would necessarily infer that the cathodic processes produce what amounts to anodic polarization.

At first sight it would seem that the concept of cathodic processes producing anodic polarization would be rather disastrous for the mixed potential theory as applied to hydrogen evolution corrosion. If the cathodic current produces anodic polarization, it would seem impossible to draw any anodic polarization curve at all for iron in acid solution which has any real significance. The true starting point for considering anodic polarization then necessarily has to be the corrosion potential since at potentials more negative the anodic cannot be separated from the cathodic effects. Mixed potential theory in its present form probably works so well because most people work with the cathodic reaction. A good explanation usually can be given for shifting the anodic polarization curve around to accommodate the picture.

With this background it would seem logical that curve 1A in Figure 8 is truly an anodic polarization curve for the oxidation of hydrogen dissolved in the steel in the corrosion process. The intersection of the extrapolation at 3.9 μ amp per sq cm would then represent the rate of re-oxidation of hydrogen at the hydrogen activity actually existing
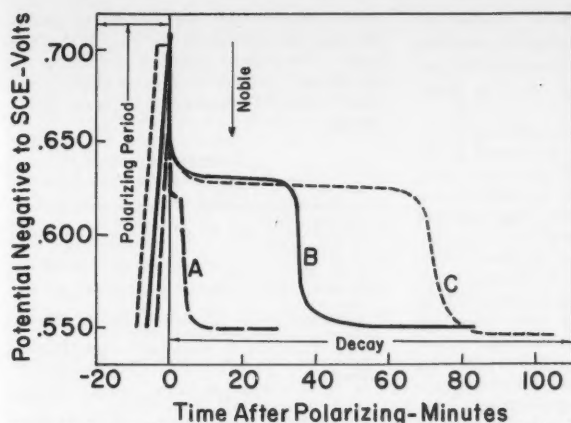
Figure 9—Potential decay curves for decoupled steel specimens cathodically polarized beyond – 0.650 volt.
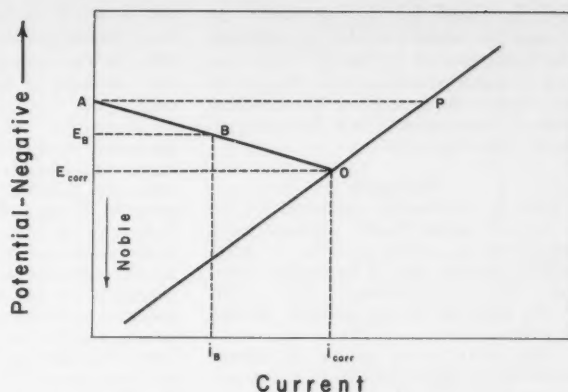

Figure 10—Determination of corrosion rate and corrosion potential by consideration of hydrogen partial reactions alone.

on the corroding specimen. The fact that a relatively rapidly determined anodic polarization curve such as this is sensitive to the oxidation of hydrogen rather than iron would indicate that the corrosion potential is purely a hydrogen potential. It indicates further that independent polarization of iron has a negligible influence in determining this potential. It has been known for years that the corrosion potential of iron in acid solution is actually a kind of hydrogen potential and this explanation substitutes a simple mechanism for a complicated one.

The next question is whether corrosion potential and corrosion rate can be uniquely determined by consideration of reactions involving hydrogen alone. As a possible alternative to the mixed potential process in establishing corrosion rate and corrosion potential, consider what happens when iron corrodes in copper sulfate solution. The cathodic process is the deposition of copper. This restricts corrosion by decreasing iron exposure until, ultimately, assuming a uniform adherent copper coating, the iron is completely covered up, corrosion is reduced to zero, and the specimen behaves as a reversible copper electrode. This is a case of a cathodic process causing anodic "polarization."

Imagine next the same thing for iron in acid solution with the assumed restriction that the reduced hydrogen behaves as a metal and no hydrogen gas is formed. Hydrogen then would plate out until iron exposure would be reduced to zero; corrosion would stop and the system would behave as a reversible hydrogen electrode with a potential as indicated by point A in Figure 10.

The activity of hydrogen would be that required to reduce the surface concentration of iron to zero. Let next a hydrogen forming process

$$H_{ads} + H^+ + \varepsilon \to H_2, \qquad (1)$$
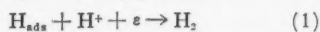
occur at a limited rate, $\frac{i_B}{2}$, by some entirely imaginary controlling mechanism. Hydrogen will then be evolved at a rate equivalent to i_B, iron will be ex-

posed and corrosion will take place. There is no question of activation control of the hydrogen evolution at this point because the assumed current, i_B, at point B is well below any such limiting rate. The potential being considered then may be visualized as a reversible hydrogen potential. Since the current i_B removes some hydrogen from the surface, the surface activity of hydrogen will be lower than at point A, resulting in a potential E_B which is more noble than the potential at point A.

It is to be emphasized that coverage by hydrogen throughout is considered as close to complete and that the area of iron exposed is very small. Thus regardless of the polarization characteristics of iron on a unit area basis, the total area of iron exposed is so small that in the range of acidities considered it has an entirely negligible effect on the potential. This assumption is justifiable only on the basis of how well the resulting hypothesis fits experimentally observable facts.

Curve AO is the locus of points, such as B, representative of the potential of hydrogen on the specimen at varying reaction rates up to the actual corrosion current. Just as with the accepted picture of the local anodic polarization curve, it does not express direct experimental reality but represents an imaginary picture. As constructed, the intersection with the activation controlled hydrogen overvoltage curve OP at point O determines the corrosion rate and the corrosion potential. It is difficult even to visualize any significance to curve AO in the area to the right of the overvoltage curve.

Curve AO expresses a relationship between potential and the rate of reaction (1). As such is may have the form of a polarization curve, but is not really a polarization curve. There is, however, another significance to curve AO. To the extent that there exists a condition in which the rate of corrosion is equivalent to the rate of hydrogen evolution it can be said that indirectly AO represents

$$i_a = f(E) \qquad (2)$$

where i_a represents the customary definition of local anodic current. On this

basis it can be considered as the "local" anodic polarization curve for the corroding specimen.

The so-called anodic polarization curve as developed in Figure 10 can be used in any manner in which such a curve is customarily used, even though its significance is different. In cathodic protection, for example, if a protective current AP is applied it will polarize the specimen to the potential of point A where the specimen will be fully protected by virtue of having exposed iron on the surface reduced to zero. At intermediate potentials the graphical analysis should be the same as with the usual interpretation. An "anodic" inhibitor becomes a substance which lowers the surface hydrogen required to reduce iron exposure to zero; any substance interfering with reaction (1) will affect both the anodic and cathodic polarization characteristics so that it is doubtful whether a truly "cathodic" inhibitor, as usually defined, actually exists for hydrogen evolution corrosion. Calculation of an anodic curve from cathodic polarization data should yield the curve AO, with no difficulties except the requirement that the curve must be of Tafel shape near the corrosion potential. Necessarily this curve will yield the proper Tafel slope for the Stern and Geary equation.[9]

As a point of difference, it is obvious that according to the analysis of Figure 10, over the range in which such an interpretation may be valid, corrosion rate will not vary with pH and the corrosion potential will have an $\frac{RT}{F}$ dependence on pH, as is observed. This is what the mixed potential concept does not explain.

Classical mixed potential theory also does not seem capable of explaining how the act of coupling steel to a more anodic material can cause a reduction in hydrogen evolution rate as well as in corrosion, accompanied by a potential shift in the noble direction. The concept of acid attack presented here does not seem incapable of yielding an explana-

tion. It would be too speculative to attempt one without further information. The interpretation to Figure 10 does not even consider time-dependent changes in polarization characteristics. The development of coupling shift is a slow process, hence time-dependent.

Summary

Steel is sacrificially protected by tin in air-free citrate buffer solution. Such protection is accompanied by a great decrease in the rate of hydrogen evolution. This is accompanied by a shift of the potential in the positive (noble) direction.

This effect is not caused by simple inhibition by dissolved tin. It is dependent upon the actual coupling of the tin and steel. For this reason the phenomenon is called "coupling shift." It has not been found possible to explain coupling shift on the basis of existing theory for the corrosion of iron or steel in weak acid media.

Polarization curves determined with automatic equipment were found to be more reproducible and accurate than otherwise possible. At a polarization speed of 25 mv per minute, reproducible Tafel-type anodic as well as cathodic polarization curves were obtained. The anodic polarization curves obtained appeared to be for hydrogen dissolved in the steel rather than for iron. The apparent absence of the iron polarization curve was taken to be an indication that the iron polarization curve has a negligible effect in determining corrosion rate and corrosion potential. It was found that corrosion rate and corrosion potential can be accounted for purely on the basis of hydrogen reaction occurring on the metal surface. Coupling shift is related to an increased hydrogen overvoltage.

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Influence of Area of the Steel Component
On Behavior of a Tin-Steel Couple*

By S. C. BRITTON and K. BRIGHT

Introduction

OBSERVATIONS WERE made[1] on the progress of corrosion of plain tinplate cans by acid fruits with a low content of depolarizers. These studies indicate an initial stage of dissolution of tin with little or no evolution of hydrogen and a final stage of rapid evolution of hydrogen accompanied by dissolution of iron. It has usually been surmised that, in the initial stage, the effective cathodic action is the reduction of depolarizers and the steel is protected partly galvanically and partly by the inhibitive effect of the dissolved tin. The final stage has been supposed to follow the exhaustion either of tin or of depolarizers. However, in the experiments of Liebmann,[1] with pure malic acid solution in cans, generally similar behavior was experienced with hydrogen evolution nil for a long initial stage. In this instance, the absence of hydrogen could not be due to the presence of depolarizers.

When the final phase is reached, the rate of hydrogen evolution for all steels is so large that the shelf-life of a can is quickly ended; therefore shelf-life is less affected by the final rate of hydrogen evolution than by the time elapsing before this rate develops. It is therefore of interest to establish the conditions in which the change from a very slow rate of hydrogen evolution to a much faster one occurs.

Abstract

Tinned steel specimens with the coating removed from selected areas have been corroded in anaerobic citric acid. Even with very small areas of exposed steel some dissolution of iron occurs, but the rate of dissolution increases sharply when the steel area is increased sufficiently to cause the current density on it to fall below an effective protective value. With small steel areas, the hydrogen produced in the corrosion process is absorbed by the steel for some weeks. The rate of hydrogen evolution increases with increased area of exposed steel but there is no sharp increase when dissolution of iron begins.

Information is given about the isolation and examination of the tin-iron alloy layer from tinplate.   5.3.2, 4.4.2, 6.3.14

From many laboratory investigations with tin-iron couples with electrodes of nearly similar size, it appears that the hydrogen evolution rate is steady and some dissolution of iron occurs. Association of constancy of hydrogen evolution rate with fixed areas of steel and tin also appeared in Vaurio's[2] experimental packing of prunes in cans for which the coating was in the form of grids or perforated sheets of tin. In these experiments the hydrogen evolution rate was greater than that in the initial stage for cans carrying the usual tin coating, but much less than that in the final stage. It appears therefore that the area of exposed steel is the main influence on the rate of hydrogen evolution and also on the rate of dissolution of iron which has appeared to be closely associated with the evolution rate.

Elementary Theoretical Treatment

Two undoubtedly important factors in the corrosion of cans, the effects of naturally occurring accelerators and inhibitors in the pack and of the tin-iron compound layer of the coating, will be ignored in this elementary treatment. The experiments of Liebmann[1] showed that the changes in rates of iron dissolution and hydrogen evolution followed the same basic pattern in a pure acid as they do in many fruit juices. Mention will be made later of the possibility that the major contribution of the tin-iron compound layer is to determine, by its structure and continuity, the area of steel that is exposed by the dissolution of a given area of the tin layer.

The very slight dissolution of iron and the persistent dissolution of tin in the early stages suggests that the system can be visualized as a wholly tin anode and a wholly steel cathode. Initially the cathode area is extremely small and the action must be largely controlled by cathode polarization.

A diagrammatic representation of the cathode and anode polarization curves is shown in Figure 1. The very steep line C represents the polarization of the small steel area initially exposed. Neglecting the effects of electrolytic resistance, the current flowing, i_1, is given by the point of intersection of the line C with the flat anode polarization curve A. If the steel area is increased by corrosion of the tin coating, the cathode polarization curve will become less steep. The changes expected, for increases in area of four times and sixteen times, are represented by the curves 4C and

16C. If the anode polarization curve were quite flat, the current density on the cathode would remain the same. Since in fact, as has been experimentally verified, there is an appreciable slope to the anode curve, the currents i_2 and i_3 given by the intersection of the two polarization curves represent a diminishing current density on the cathode. This diminution of cathode current density will be accentuated if the tin area sensibly diminishes with a consequent increase in the slope of the anode polarization curve. Ultimately the current density on the cathode must fall to a value at which the dissolution of iron is no longer prevented and the situation becomes complicated by the operation of anodes on the steel.

On the argument put forward, the hydrogen evolution rate should initially be very low because of the limitation on current flow imposed by the small cathode area; but it should be finite. This stage could last a long time because the exposure of more steel has to await dissolution of parts of the tin coating. When once the exposed steel area begins to increase, the process will be an accelerating one; increase in area of exposed steel increases the rate of dissolution of tin which increases the rate of exposure of steel. The sudden increase in hydrogen evolution rate and the commencement of appreciable dissolution of steel may therefore both be consequences of the rapid extension of the steel area and their association may be coincidental. There is no obvious reason why the transfer of part of the anodic action from tin to steel should immediately accelerate hydrogen evolution.

The main objects of the present research are to establish under the simplest possible conditions that the surmises just made have some foundation. In particular it is desired to establish what may cause sharp increases in the rates of iron dissolution and hydrogen evolution, and why hydrogen evolution in the early stages is often not detected.

In the rather simplified outline given, no mention has been made of the important effect of dissolved tin. From the observed effect on polarization curves for tin and steel, it appears likely that dissolved tin does not affect the nature of the electro-chemical process discussed but that it reduces current flow, other things being equal. Certainly in view of its known ability to act as an anodic inhibitor of the corrosion of steel, as shown by Hoar and Havenhand,[3] it must be expected to reduce the current density on steel necessary to repress anodic action. Part of the research undertaken has been devoted to demonstration of some of the effects of dissolved tin.
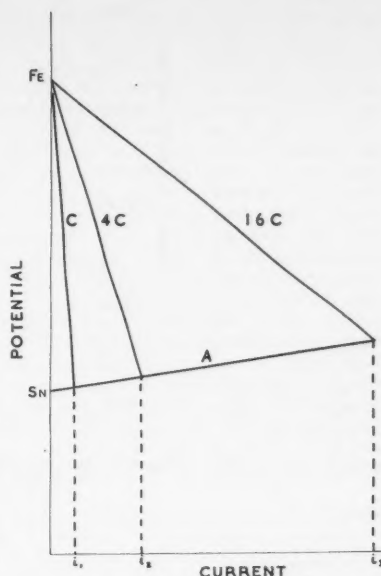
Figure 1—Diagrammatic representation of the increase in current flow expected as the steel area increases from its initial value by 4 and 16 times with the tin area remaining constant.

Experimental

The research is still in progress and the results of only part of it will now be reported. This part is concerned with the examination for immersion in anaerobic citric acid of:

1. The relation of the rate of hydrogen evolution to the area of exposed steel in an incomplete tin coating.

2. The existence of a "protective current density" for tinplate base steel.

3. The variation of the corroding potential with area of exposed steel in an incomplete tin coating.

4. The effects of the tin-iron compound layer.

For all of these examinations except No. 4, the presence of a tin-iron compound layer has been avoided; tin coatings on steel have been produced by electro-depositing tin from the stannous sulfate, cresol-sulfonic acid bath with additions of gelatin and β naphthol. For experiments with discontinuous coatings, the whole steel surface was first plated. Then the areas of coating to be retained for the experiment were protected by wax and the coating was removed from the remaining area by anodic dissolution in caustic soda solution. Finally the wax protection was removed leaving the specimen with areas of clean tin and steel. Each individual area of exposed steel was about 5x5mm. Larger total areas of steel were obtained by stripping the
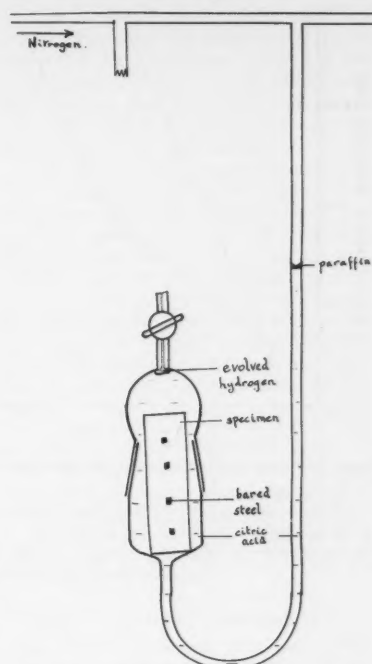
Figure 2—Cell used for hydrogen evolution experiments.

required number of the small areas distributed, as far as possible, uniformly over the specimen. The bared areas were measured before use of the specimens in experiment, in order to take account of any imperfect masking. The two steels used had the rolling and annealing treatments of tinplate base steels. They were generally similar but the copper contents were 0.04 percent for steel A and 0.11 percent for steel B.

In order to avoid the effect of possible variations in the surface layers of the steels, the specimens were chemically polished before heating using the method of Marshall.[4] Immersion was for 15 seconds at 65 C in 0.3M oxalic acid + 0.5M hydrogen peroxide; this removed a depth of about 10^{-5} inch and left a smooth surface uniform in appearance.

The experiments have been made in oxygen-free 0.1M citric acid solution under nitrogen. When dissolved tin was deliberately added to the solution it was in the form of stannous citrate.

Hydrogen Evolution

Specimens of Steel A of size 7x2cm were plated with tin and areas of the

TABLE 2—Hydrogen Evolution Rates (Measured from Start of Visible Evolution) for 7 x 2 cm Partially tinned steel specimens in De-aerated 0.1 M Citric Acid at 25 C

Area of Exposed Steel as Percentage of Total Area	Hydrogen Evolution Rate, ml/100 days
Pores only	0.17
1	0.12
5	0.21
10	0.26
20	0.45
50	5.4

TABLE 1—Dissolution of Tin and Iron from 7 x 2 cm Partially De-tinned Specimens in De-aerated 0.1 M Citric Acid in 40 Days at 25 C

Percentage of Specimen Area on Bare Steel.	Iron Dissolved, mg	Tin Dissolved, mg	Calculated Average Current, µ Amp	Current Density on Steel, µ Amp/cm².
1	0.03	0.25	0.125	0.46
10	0.03	2	1.0	0.37
25	0.23	3	1.5	0.22
50	0.44	7.3	3.7	0.27

mens with very small areas of steel exposed. With steel exposed only at pores in the tin coating, hydrogen became visible after about 150 days; with 1 percent of the area as steel, the time required was about 75 days. When evolution once became visible, the hydrogen accumulated slowly but steadily. The rates of evolution, measured from the observed start, for different areas of exposed steel were as shown in Table 2.

For increase in the area of exposed steel up to 20 percent of the total area, there was thus a gradual rise in the rate of hydrogen evolution, but for the change from 20 to 50 percent, there was a large rise. It appears from the results of the first experiment (Figure 3) that the transition from coatings 50 percent complete to bare steel produces no further sharp change if, as is proper, the bare steel in a solution containing dissolved tin is considered.

There is no suggestion of a sudden increase in hydrogen evolution at the stage of de-tinning (10-25 percent) found in the first experiment to be associated with increased iron dissolution. The second experiment is still in progress, so that direct comparison of hydrogen evolution and iron dissolution in the most interesting range is not yet possible.

The protection of the steel by applied current has however been studied in other ways.

Protective Current Density

It is commonly found, and is indeed to be expected that complete prevention of metal dissolution by cathodic treatment does not occur in acid solution. It is however possible to establish conditions in which the solid metal is in equilibrium with a very dilute solution of its ions and the current density then applied is effectively protective because dissolution ceases.

Steel specimens, after surface preparation, were masked with wax to give an exposed area of 10 sq. cm. and placed in cells with the exposed surface opposing a platinum electrode. With connections made through battery, variable high resistance and micro-ammeter to make the steel the cathode and the platinum electrode the anode, 100 ml deaerated 0.1M citric acid was introduced. Current was allowed to flow for 30 minutes and the amount of iron dissolved was then estimated by analysis of the solution. The experiment was then repeated for a different value of cathodic current density.

At any values of current density, some iron passed into solution, but above a limiting value, the amounts of iron in solution remained at about 0.25 ppm independent of current density and of period of immersion. Typical curves showing the relation, at the end of 30 minute experiments, between dissolved iron and applied current density are shown in Figure 4. Both curves shown relate to Steel B, chemically polished; for one the solution was tin-free and for the other the solution contained a 0.001M addition of stannous citrate. The limiting current density for restraint of

iron solution was, in the absence of tin ions, of the order of $100 \mu \text{Amp/cm}^2$.

In the solution 0.001M in stannous citrate the protective current was of the order of $10 \mu \text{Amp/cm}^2$. It was diminished still further at higher tin concentrations but precise measurement at the small current densities was not possible. The current density suggested earlier for protection of the steel in the hydrogen evolution experiments was $0.4 \mu \text{Amp/cm}^2$. This is of a different order from the values directly measured, a fact possibly accounted for by the high tin ion concentration at the surface of the corroding tinned steel specimens. The limiting values of iron concentration at which further dissolution ceases when the protective current is applied were of the same order for the hydrogen evolution experiment (0.6 ppm) and for the applied current experiment (0.25 ppm).

The relationship of current density to iron solution was obtained consistently for the steels A and B and for different methods of surface preparation. Any difference in the limiting current densities for the two steels was less than could be perceived by the technique used.

According to the hypothesis advanced, the corroding potential of tinned steel should change gradually with increase of the exposed steel area until the current density on the steel falls below a protective value. As illustrated in Figure 1, the potential should, until this stage is reached, follow the anodic polarization curve for tin which will only gradually change in slope as the tin area is reduced. At the point at which steel is no longer protected, the potential might be expected to move abruptly as iron anodes come into action.

Specimens of tinned steel of size 7 x 2cm. were prepared as for the hydrogen evolution experiment by plating with tin and removing the coating from selected areas. Each specimen was placed in a glass cell filled with 0.1M. citric acid. A capillary filled with the test solution led from each cell to a central reservoir from which connection was made via a salt bridge to a saturated calomel electrode. The potentials, measured at 25 C, were initially unsteady but stability was reached after about 24 hours and a relationship between potential and area of exposed steel was obtained such as is illustrated in Figure 5. There was a small but consistent difference between the corroding potentials of specimens with small and large areas of exposed steel and the change occurred with some abruptness at an exposed steel area about 10 percent of that of the specimen. One experiment was allowed to continue for 24 days and the iron contents of the solutions were then estimated with the results shown in Table 3.

The maximum protected steel area of about 10 percent of the specimen area was similar to that found in the hydrogen evolution experiment. The iron content of solutions in the "protected" range was 0.1 - 0.2 ppm as compared with 0.6 ppm in the hydrogen evolution experiment and 0.25 ppm in protection by

applied current. Perfect agreement is not to be expected in experiments made under differing conditions since it is the concentration of iron at the metal/solution interface that must be the determining factor, and it is satisfactory that the values are of the same order.

Although the small changes of potential call for highly precise measurement, they promise to make the comparison of the protective power of tin for different steels rather easier than in the method with applied current. This method required large numbers of specimens and of solution analyses. It may however be possible to apply a current to give variation of current density over one specimen and, by measuring the variation of potential over it, to assess the current density at which protection ceases. An attempt to use a long steel strip cathodically polarized by current from an anode opposite one of its ends, as in the method described by Bruckner[5] for the study of the cathodic protection of lead, was not successful. Other methods are being explored.

Effect of Tin-Iron Compound Layer

Practical experience has not given conclusive evidence of the effect on the corrosion of tinplate of variation in the amount of tin-iron compound in the coating. There is however good evidence that the quality of the compound layer is strongly influential; some experiments have been made to explore the probable effects.

The method described previously[6] for the isolation of pieces of the compound layer has been improved somewhat in detail although basically it remains a process of uniform dissolution of the steel base of tinplate by stages which become increasingly more cautious as the compound layer is approached. The stages, starting with tinplate, are as follows:

1. Coat one face and the edges of the sample with wax and immerse in concentrated hydrochloric acid containing antimony trichloride until tin and alloy are removed from the exposed face.

2. Immerse the sample in 1:1 nitric acid at about 30 C until about 75 percent of the steel is removed. Then rinse.

3. Immerse in a chemical polishing solution (0.3M oxalic acid and 0.5M hydrogen peroxide) at 30-40 C. Continue treatment (2-4 hour) until a small grey spot of alloy appears. Remove and rinse.

4. Immerse in a suspension of 1 gm gum tragacanth and 50 gm finely divided sulfur in 100 ml of chloride-free water. Leave for a day or two until all steel is removed. Wash and dry.

5. Coat the exposed alloy with a lacquer resistant to both alkali and wax solvent. Cold setting Araldite resin is suitable and handling of the now fragile sample is enhanced if a glass plate is sealed over the surface.

6. Remove with solvent the initial wax coating and dissolve the tin from the surface now exposed in sodium plumbite solution at 80 C. Wash away the precipitated lead. The immersion should not

be unduly prolonged since the alloy may be slowly attacked by the plumbite solution.

An alternative procedure, which is preferred for electrolytic tinplate is to remove the tin layer by anodic treatment in NaOH solution as the first step. The exposed alloy is then covered as in stage 5 and the other face of the tinplate is attacked by the sequence of treatments 1 to 4.

By this method areas of around 100 sq. cm. have been isolated from hot-dipped tinplate. From electrolytic tinplate however only fragments have been isolated and the observations made suggest that the layer is in fact uneven and discontinuous.

The corroding potential of the isolated alloy was much more noble than that of tin or steel. Potentials 300-400mV more positive than those of tin and steel were observed in 0.1M potassium chloride, aerated, or in 0.1M citric acid, aerated or de-aerated. This difference is considerably larger than that observed by Covert and Uhlig[7] using compound specially prepared by immersing iron in molten tin, but enoblement, especially in aerated solution, occurs as immersion time is prolonged.

Current flow in couples of the alloy with tin and steel was well maintained in aerated but not in de-aerated solutions. In de-aerated 0.1M citric acid, tin was corroded faster when coupled to alloy than when immersed alone but slower than when it was coupled to steel. Corrosion of the alloy either immersed alone or coupled was insignificant. Covert and Uhlig obtained somewhat similar results in tests of artificially produced alloy and attributed the inertness of the alloy as cathode to its high hydrogen overpotential.

Perhaps, in a solution free from oxygen or other cathode depolarizers, the compound layer may be best visualized as an almost inert barrier. In this character it could however exercise a considerable influence since its degree of continuity will decide the area of steel which is exposed by the dissolution of tin layer. If this is so, the *form* rather than the *amount* of the compound layer may be the basis of its effects and this may account for some inconsistency in the observed effects of amount. Although there is some association between form and amount, it is by no means rigid. C. J. Thwaites has obtained, from examination of taper sections, good evidence of the dependence on surface condition of the steel of the form and continuity of similar quantities of compound layer on electrolytic tinplate.

Discussion and Conclusions

The information obtained gives support to the view that the changes in rates of hydrogen evolution and of iron dissolution, observed as corrosion progress in a plain tinplate can of acid fruit of low depolarizer content, results from increasing exposure of the steel by dissolution of the tin coating. It has been shown that small areas of exposed steel in citric acid solution can be protected by contact with tin and that, for the steel used and *for an unalloyed tin coating*, this protection breaks down when about 10 percent of the steel area is exposed. It has also been shown that the current density which has to be maintained on the steel to protect it is about $100~\mu$ Amp/sq. cm. in a tin-free solution but possibly less than $1~\mu$ Amp/sq. cm^2 in a solution containing dissolved tin. Protection is not complete but dissolution of iron ceases effectively when the iron content of the solution is about 0.3 ppm.

Evidence has not been found that the rate of hydrogen evolution increases with special sharpness when continued iron dissolution becomes apparent. It appears that the area of exposed steel required for rapid hydrogen evolution is appreciably greater than that which can be protected by the couple current. The divergence from the observations made on cans that hydrogen evolution and iron dissolution go together may result from the difference in conditions of observation. In any one experiment the steel area was fixed; in the tinplate container however, an area of steel once exposed is likely to expand at an accelerating rate. If, as is suggested, dissolution of iron begins with an exposed steel area of about 10 percent, this will be one stage in a situation changing so rapidly that, with the imprecise observations possible on a can, it may seem to mark the beginning of the change.

If the start of iron dissolution has a precise relation to hydrogen evolution, the protective current density for a particular steel would have special importance; further work may show whether this is so. In any event the existence of a protective current density probably has some bearing on the choice of conditions for tests of tinplate. It appears extremely likely that the rate of loss of the tin coating up to the stage when bare areas of steel appear is all important. Up to that stage the rate depends on the action of any depolarizers present and on the cathode efficiency of steel exposed at pores and scratches in the coating. The best hope of a rapid estimate of the expected rate of de-tinning for a particular steel should be from the current generated between tin and the steel base, provided that the area of the steel is sufficiently small to ensure that it is wholly cathodic (i.e., the current density exceeds the protective value).

If it is right to regard the compound layer as an inert screen to the steel, then the stage at which exposure of steel by dissolution of tin begins to produce serious acceleration of the corrosion process will depend on the continuity of the layer. The promising Alloy-Tin Couple Test devised by Kamm, in which the current passing between tin and tinplate stripped of its tin layer is measured, may be providing an indication both of the continuity of the compound layer and of the cathodic efficiency of the steel exposed at discontinuities.

The effects, in fruit juices, of depolarizers on de-tinning without stimulus from cathodic action of steel and possibly on the action of the tin-iron compound layer, and of substances which affect the cathode behavior of the steel make it unlikely that a test carried out in one fruit juice will give results applicable to other types of juice. Likewise the conclusions of the work now described must be considered of limited application but it is hoped that they will help interpretation of observations made in other conditions.

The conclusions, for corrosion in oxygen-free citric acid are as follows:

1. Dissolution of iron from unalloyed tinned steel appears to occur continuously only when the exposed steel area is above a limiting value. With areas below this value there is an initial slight dissolution which does not continue. The limiting area in 0.1M citric acid was about one-tenth of the tin area.

2. With applied cathodic polarization, dissolution of iron from steel in 0.1M citric acid occurs continuously only when the current is below a limiting value. The limiting value for the steel used, was, in the absence of tin ions, about $100~\mu$ Amp/sq. cm. In the presence of 0.001M tin salt it was about one-tenth of this and probably less still under some conditions.

3. Visible hydrogen evolution from tinned steel with small areas of the steel exposed may be delayed for many weeks during which time the steel is absorbing hydrogen. When visible evolution commences, its rate depends on the area of bare steel exposed, increasing slowly but steadily until 20 percent of the surface is steel and then rising more rapidly for further increases of exposed steel area.

4. The layer of tin-iron compound in the coating on tinplate is cathodic to tin and to steel but does not seriously stimulate the corrosion of steel in anaerobic conditions. Its continuity is variable with possible important effects on the area of steel exposed by dissolution of tin.
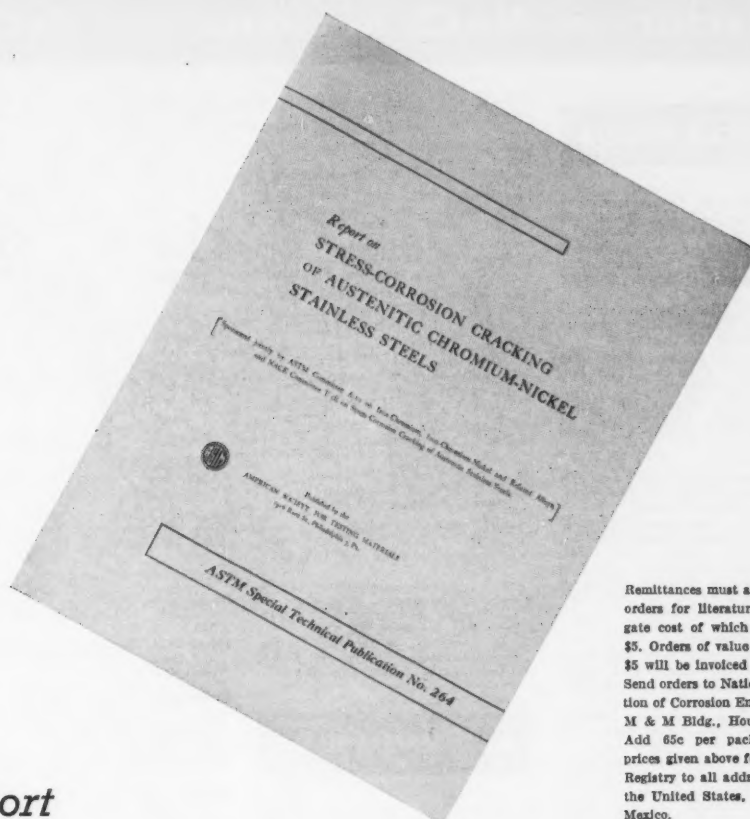
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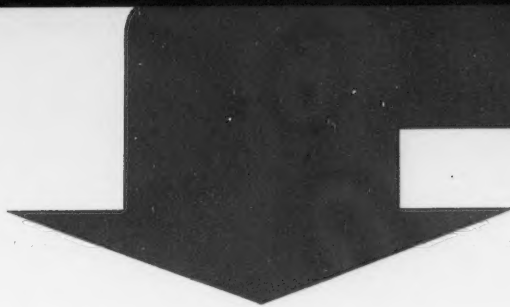
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E	3" x 60"	4.0	115	Salt Water
G	2" x 9"	0.4	5	Ducts
J	3" x 36"	2.5	80	Salt Water
M	2" x 60"	2.8	57	Salt Water

*Applicable also in fresh water service. Should not be used in ground beds without backfill.

DURCO

THE DURIRON COMPANY, INC. / DAYTON 1, OHIO